

CONTRIBUTIONS
FROM
THE PHYSICAL LABORATORY
OF
THE UNIVERSITY OF MICHIGAN

Number 4

1. A. H. Stang: The Infra-Red Absorption Spectrum of Naphthalene and of Some of Its Mono-Derivates in Solution.
(Reprinted from *The Physical Review*, June, 1917.)
2. D. L. Rich: Oscillatory Spark Discharges Between Unlike Metals.
(Reprinted from *The Physical Review*, August, 1917.)
3. Arthur Whitmore Smith: Demagnetization of Iron.
(Reprinted from *The Physical Review*, September, 1917.)
4. Charles F. Meyer: The Wave-Length of Light from the Spark Which Excites Fluorescence in Nitrogen.
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5. Winthrop R. Wright: The Magnetization of Iron in the Absence of Hysteresis.
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6. W. W. Sleater: The Absorption of Near Infra-Red Radiation by Water-Vapor.
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7. H. M. Randall and E. F. Barker: The Infra-Red Arc Spectrum of Iron.
(Reprinted from *The Astrophysical Journal*, January, 1919.)
8. H. M. Randall and E. F. Barker: The Infra-Red Arc Spectra of Cobalt, Nickel, Manganese, and Chromium.
(Reprinted from *The Astrophysical Journal*, January, 1919.)

Ann Arbor, Mich.
April, 1919

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FOREWORD

THE CONTRIBUTIONS FROM THE PHYSICAL LABORATORY are sent now for the first time to a number of Libraries and Universities. It is regretted that the preceding numbers of the CONTRIBUTIONS cannot also be supplied. To compensate partially for this there are reproduced below the lists of papers contained in the earlier numbers. The references will make it possible to find the original papers in the Journals where they are published.

Number 1

April, 1913

1. A. W. Smith: Heat of Evaporation of Water.
(Reprinted from *The Physical Review*, September, 1911.)
 2. A. G. Worthing: Some Thermodynamic Properties of Air and of Carbon Dioxide.
(Reprinted from *The Physical Review*, October, 1911.)
 3. H. M. Randall: Residual Rays of Selenite.
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 4. J. E. Harris: The Elastic Properties of Bismuth Wires.
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 5. J. T. Littleton: Notes on Optical Constants of Metals.
(Reprinted from *The Physical Review*, October, 1912.)
 6. P. Field, On Coulomb's Laws of Friction.
(Reprinted from *Zeitsch. f. Math. u. Physik*, December, 1912.)
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March, 1915

1. F. A. Osborn: Change of Index of Refraction of Water with Change of Temperature.
(Reprinted from *The Physical Review*, March, 1913.)
2. P. Field: On Constrained Motion.
(Reprinted from *Zeitschr. f. Math. und Physik*, March, 1913.)
3. N. H. Williams: The Stability of Residual Magnetism.
(Reprinted from *The Physical Review*, May, 1913.)
4. N. H. Williams: Anomalous Temperature Effects Upon Magnetized Steel.
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5. C. W. Green: Polarization of the Aluminium Rectifier.
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6. G. A. Lindsay: A Study of the Longitudinal Vibration of Wires.
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7. K. E. Guthe: Roger Bacon as a Scientist.
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THE INFRA-RED ABSORPTION SPECTRUM
OF NAPHTHALENE AND OF SOME
OF ITS MONO-DERIVATIVES
IN SOLUTION

BY A. H. STANG

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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THE INFRA-RED ABSORPTION SPECTRUM OF NAPHTHALENE AND OF SOME OF ITS MONO-DERIVATIVES IN SOLUTION.

BY A. H. STANG.

INTRODUCTION.

ALTHOUGH much experimental work has already been done on finding the infra-red absorption spectrum of different substances, there remains a very large number of substances whose spectrum is unknown. The results of the infra-red investigations have been very fruitful in solving problems of molecular structure and in testing the energy quantum theory, especially as applied to the theory of specific heats. Thus Bjerrum¹ from a knowledge of the infra-red absorption bands of CO₂ has proposed a solution for the problem of the arrangement of the atoms in the CO₂ molecule, while Nernst and Lindemann² have deduced formulas for the variation of the specific heat with temperature that agree closely with experimental data and are based on the location of infra-red absorption bands of the substances in question.

Still more recently Baly,³ of the University of Liverpool, has proposed a theory which unites the absorption of an organic substance in the infra-red to that in the visible and ultra-violet regions of the spectrum and to the fluorescence and phosphorescence which a body may emit. He has, in particular, predicted from theoretical considerations at what wave-lengths the infra-red absorption maxima of several substances should occur. Among these substances was naphthalene, C₁₀H₈.

The object of this paper is then to investigate the absorption of naphthalene as well as that of several of its mono-derivatives and especially to obtain the positions of maxima absorption. Since these substances are solids at ordinary temperatures, it was determined to obtain their absorption curves when in solutions of carbon disulphide and carbon tetrachloride. These solvents were chosen because they are relatively transparent in the infra-red. From these absorption curves the effect of the solvent and of isomerism will be noted. The agreement of these

¹ Bjerrum, Verh. der deut. Phys. Gesell., 16, p. 737, 1914.

² Zeit. für Electro-chemie, 17, p. 867, 1911.

³ Baly, Astro-phys. Journal, 42, p. 4, 1915. Phil. Mag., Vol. 27, p. 632, 1914; vol. 29, p. 223, 1915; vol. 30, p. 510, 1915; vol. 31, p. 417.

absorption maxima with Baly's theory of absorption will also be tested and some conclusions as to the validity of that theory drawn.

APPARATUS.

A fixed arm spectrometer, provided with the Wadsworth¹ constant minimum deviation attachment was used for the work. Fig. 1 gives a diagram of the apparatus. *A* is an adjustable slit. *B* and *E* are 9 cm. diam. 50 cm. focal length spherical mirrors, silvered on the outside. *C* is a rock salt prism, 8 cm. along each face and 8 cm. high, with a refracting angle of $59^{\circ} 58'.75$, obtained from Brashear. The prism was protected from moisture by having a small dish of anhydrous calcium chloride placed upon it and several others on the spectrometer, which was enclosed in a blackened case. When not in use, the prism was covered with a bristol board box painted inside with paraffine which fitted closely to the spectrometer table. The small weight of this box made it preferable to a heavy glass bell-jar. *D* is the Wadsworth plane mirror, while *F* is a plane 10×10 cm. mirror used to change the direction of the convergent light from *E* so that the filar microscope *J* could be used for reading the 35 cm. diam. circle *K*. *G* is a Rubens thermopile, made up of iron constantin junctions with a fixed slit width of 0.03 cm. A Leeds and Northrup sensitive galvanometer was used on closed circuit in series with the thermopile. The source of radiation *L* was a 220-volt Nernst glower. A spherical mirror *M* focused the light on the slit.

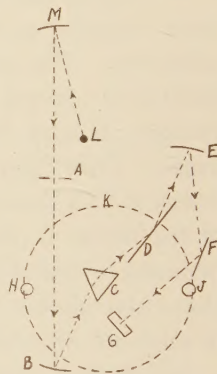


Fig. 1.

The cells used to hold the solutions were made of two plates of polished rock salt about $2 \times 4 \times .4$ cm., between which a clean copper wire bent in U shape was placed. After the plates had been finally polished on an optical grinder with rouge and absolute alcohol, the wire was placed between them and cemented to the plates with SiO_2 . The solvents used did not attack any of the materials in the cell. After filling the cell, a glass plate was cemented over the top to prevent evaporation.

A thin wooden block that ran in vertical ways between stops was provided with two openings somewhat smaller than the cells. The cell containing the solution to be investigated was placed over the upper opening. Over the lower opening a duplicate cell, having the same absorption when empty, was placed filled with the pure solvent. The

¹ Wadsworth, Phil. Mag. (5), 38, p. 346, 1894.

elevator was so placed that the cells could be brought in succession exactly to the same position in front of and close to the slit. Between the elevator and mirror *M* interposed a metal screen which could be operated by the observer.

The naphthalene used was recrystallized from alcohol. The beta naphthylamine was obtained from Merck and Co. The alpha and beta naphthol, the nitronaphthalene and the alpha naphthylamine were very kindly furnished by Professor M. Gomberg of the chemistry department. The solvents were obtained from stock in the laboratory. They were listed as c.p. but since the absorption of the solvents does not enter into the final result, absolute purity is not necessary.

PROCEDURE.

A calibration curve for the rock salt prism was made from values given by Paschen.¹ Since the observation room was always kept at 25° C. the values of the refractive index were corrected for temperature by his correction formula.

Before each set of observations, the instrument was calibrated with an optical setting on the .546 μ Hg line and then tested with the Bunsen flame emission maximum which has been accurately located² at 4.40 μ . From the calibration curve, this maximum was always found at a wavelength smaller than 4.4 μ by about 0.4 minute of arc. This discrepancy has been noticed by several investigators³ who attribute it variously to curvature of the image of the slit and to a real difference between a bolometric and an optical setting of the standard line on the slit. Correction was made by assuming that the Bunsen maximum was at 4.400 μ and displacing the calibration curve by the required amount. It may be noted that the .03 cm. width of slit for a 50 cm. focal length mirror amounts to 2.03 minutes of arc.

After the cells had been placed on the elevator and the zero galvanometer reading taken, the metal screen was raised so that light could pass through the cell which contained the solution. When the maximum deflection had been noted, the elevator was raised until the cell containing the solvent came in front of the slit. The deflection now increased and finally came to rest at a value larger than the first. With a linear thermopile such as was used the percentage of energy transmitted was computed by finding the ratio of the deflection through the solution to that through the solvent.

In general, readings were taken one minute apart on the spectrometer

¹ Paschen, *Ann. der Physik*, 26, p. 120.

² Paschen, *Wied. Ann.*, 52, p. 209, 1894; 53, p. 337, 1894; 60, p. 714, 1897.

³ Coblenz, *Carnegie Inst. Publ.*, No. 35, p. 20. Paschen, *Wied. Ann.*, 52, p. 209, 1894.

circle but in the neighborhood of an absorption band they were taken closer together so as to accurately locate the minimum of transmission. Table I. is a sample taken at random from observations through one absorption band. It shows the variation of the intensity of the light caused by the absorption of the solute and of the solvent and by the Nernst glower.

TABLE I.

Infra-red Absorption Data. α Nitronaphthalene in CS_2 .

1. Angle from $\lambda = .546\mu.$	2. Wave-length.	3. Solution Deflection, Cm.	4. Solvent Deflection, Cm.	5. Per Cent. Transmitted.
37.00	7.070 μ	1.49	2.01	74.0
38.00	7.160	1.79	3.19	56.1
39.00	7.250	1.42	4.12	33.4
40.00	7.334	1.04	4.58	22.7
40.32	7.360	.93	4.83	19.2
40.62	7.384	.87	4.97	17.5
41.00	7.415	.79	4.93	16.0
41.33	7.440	.84	5.03	16.7
41.61	7.463	.89	5.04	17.7
42.00	7.493	1.00	5.00	20.0
43.00	7.571	1.76	4.95	35.6

The minimum of transmission was always determined from a plot made on a large scale of several values near the minimum. The point where the two lines (Fig. 2) meet was taken as the position of maximum

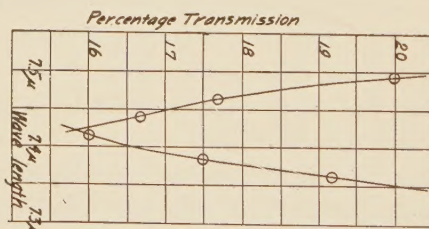


Fig. 2.

α Nitronaphthalene Absorption Band in CS_2 at 7.42 μ .

absorption. No correction has been made for finite slit width and impurity of the spectrum. Several bands were plotted to an enlarged scale and the correction method proposed by Runge¹ applied. The corrected absorption curve was indeed deeper but there was no shift of the position of the maximum comparable to the experimental error.

In the tables giving the positions of maximum absorption are given

¹ Runge, Zeit. für Math. und Phys., 42, p. 205, 1897.

the estimated limits of error in location after account has been taken of errors that may arise in percentage transmission, plot, calibration curve, adjustment test, and change in temperature.

CHEMICAL STRUCTURE OF NAPHTHALENE AND OF ITS DERIVATIVES.

Naphthalene, $C_{10}H_8$ ¹ consists of two benzene nuclei which have in common two carbon atoms. The accepted formula is given in Fig. 3. The replacement of an H atom in naphthalene gives rise to two isometric mono-derivatives. They are called either α or β derivatives according as the substituent is adjacent to the complex of Fig. 4, common to both groups, or separated from it by a CH group.

α naphthol, $C_{10}H_7(OH) + H_2O$ is represented by the formula of Fig. 5

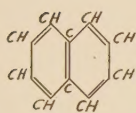


Fig. 3.



Fig. 4.

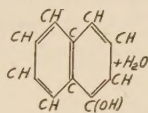


Fig. 5.

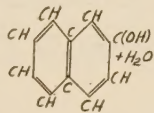


Fig. 6.

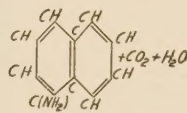


Fig. 7.

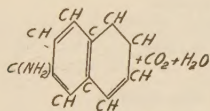


Fig. 8.

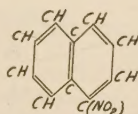


Fig. 9.

Fig. 3. Naphthalene.

Fig. 5. α Naphthol.

Fig. 6. β Naphthol.

Fig. 7. α Naphthylamine.

Fig. 8. β Naphthylamine.

Fig. 9. α Nitronaphthalene.

while β naphthol is shown in Fig. 6. The α and β naphthylamine $C_{10}H_7(NH_2) + CO_2 + H_2O$ correspond to Figs. 7 and 8 respectively and α nitronaphthalene $C_{10}H_7(NO_2)$ has the formula of Fig. 9.

DISCUSSION OF THE RESULTS.

In Fig. 10 are given the transmission curves for naphthalene in CS_2 and in CCl_4 respectively. Table II. gives the location of the absorption maxima. The CS_2 solution gives more bands but except for the band at 3.30μ the location of the common bands agrees within experimental error. Coblenz² has investigated the absorption of naphthalene in CCl_4 in this region and found a band at 3.25μ . The CS_2 band was however located at 3.30μ in several solutions, the observations having been taken more than two months apart. This shift from 3.25μ to 3.30μ must be due to the effect of the solvent itself.

¹ Richter-Smith, Organic Chemistry, vol. 2, p. 390, 1900.

² Coblenz, *loc. cit.*

Since naphthalene consists of two benzene nuclei, it will be of interest to note that Coblenz has found absorption maxima of benzene at $2.7\ \mu$, $3.25\ \mu$, $4.4\ \mu$, $4.9\ \mu$, $5.5\ \mu$, $6.2\ \mu$, $6.75\ \mu$, $7.25\ \mu$, $7.8\ \mu$, $8.67\ \mu$, and $9.78\ \mu$.

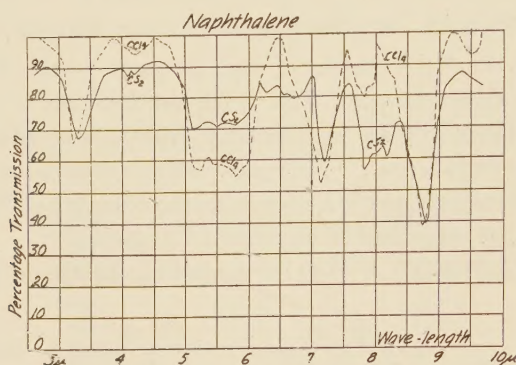


Fig. 10.

TABLE II.

Naphthalene Absorption Maxima.

No.	In CS ₂ .	In CCl ₄ .	Wave No.
1	$3.30\mu \pm .03\mu$	$3.25\mu \pm .03\mu$	308
2	4.2 .10	4.22 .04	237
3	5.15 .10		194
4		5.27 .03	190
5	5.5 .10		182
6	5.8 .10	5.80 .02	172
7	6.31 .02		159
8	6.75 .10		148
9	7.20 .03	7.18 .03	139
10	7.84 .02	7.84 .03	127
11	8.18 .02		122
12	8.79 .02	8.78 .02	114
13	9.81 .03		102

It is to be noticed that many naphthalene bands occur at the same wave-lengths. These must be due to the vibration of the benzene ring, still present in the naphthalene and are not characteristic of the naphthalene itself.

Baly¹ in his theory has arrived at the conclusion that the wave numbers of the absorption band in the visible or ultra-violet region of the spectrum should be equal to the product of the wave numbers of several infra-red bands by whole numbers. Such a test would serve as a criterion of the worth of his theory. For example, Russel and Lapraik² found three

¹ Baly, *loc. cit.*

² Chem. Soc. of Lon. Trans., 39, p. 171, 1881.

naphthalene absorption bands, the maximum absorption occurring from .714 μ to .707 μ , from .636 μ to .634 μ , and from .619 μ to .611 μ while the mean wave numbers for these bands are 1407, 1571, and 1626 respectively. The wave numbers of the infra-red bands giving closest agree-

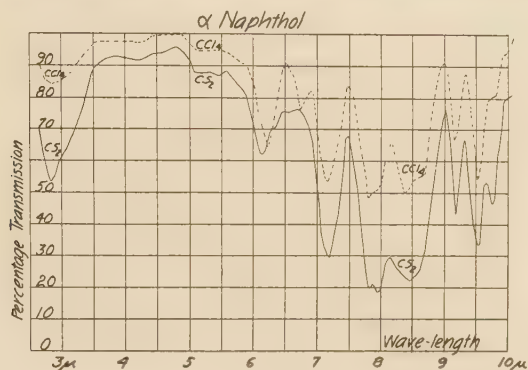


Fig. 11.

TABLE III.

Infra-red Absorption Maxima. Alpha Naphthol.

1.	2.	3.	4.	5.	6.	7.
No.	In CS ₂ .		In CCl ₄ .		Wave No.	
1	2.85 μ ± .03 μ		2.87 μ ± .04 μ		286	
2	6.15 .02				162	D
3			6.24 .03		160	
4			6.76 .03		148	ND
5	7.19	.03	7.19	.03	139	ND
6	7.84	.03	7.82	.03	127	ND
7	7.97	.03			125	
8	8.44	.04	8.40	.03	119	D
9	9.17	.02	9.17	.02	109	
10	9.54	.03	9.54	.02	105	
11	9.73	.03			103	D

Purvis at 3068 (2, 5, 6, 9, 11); at 3324 (5, 6, 8).

ment are for 1407, $139 \times 10 = 1390$, $127 \times 11 = 1397$, $238 \times 6 = 1428$; for 1571 there are no close values; for 1626, $102 \times 16 = 1632$, and $148 \times 11 = 1628$.

The wave numbers of the other bands found by various investigators in the visible region are given below. The numbers in parenthesis after each wave number refer to the infra-red bands listed in Table II. which are very nearly integral factors of this visible wave number.

By Hartley¹ at 3504 (4, 7); at 3670 (4, 7, 11, 13); at 3801 (3, 6, 7, 11); and at 3922 (2, 11).

¹ Chem. Soc. of Lon. Trans., 47, p. 685, 1885.

By Baly and Tuck¹ at 3125 (4, 8); at 3222 (9); at 3700 (1, 4, 8, 10).

By Guthrie² at 3102 (4, 5, 6, 8); at 3167 (7, 11, 13); at 3207 (9, 12); at 3306 (2, 3, 4, 10, 11, 12); at 3488 (4, 7, 9); at 3574 (10, 13); at 3625 (5, 6, 9); and at 3745 (9, 12).

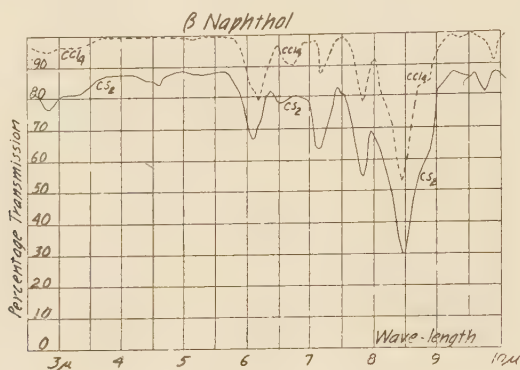


Fig. 12.

TABLE IV.

Infra-red Absorption Maxima. Beta Naphthol.

1. No.	2. In CS ₂ .	3.	4. In CCl ₄ .	5.	6. Wave No.	7.
1			2.77μ ± .10μ		361	
2	2.87μ ± .04μ				350	
3	6.12 .03		6.18 .03		163	D
4	6.5 .10				154	
5			6.75 .03		148	ND
6	7.18 .03		7.21 .02		139	ND
7	7.84 .02		7.85 .03		128	ND
8	8.47 .02		8.47 .02		118	D
9	9.72 .02				103	D
10			9.90 .06		101	

Purvis at 2996 (8) at 3712 (4, 5, 7, 9).

¹ Purvis, Chem. Soc. of Lon. Trans., 101, p. 1315, 1912.

From these results it is seen that nearly all of the absorption maxima in the visible and ultra-violet have wave numbers which are integral multiples of several infra-red absorption wave numbers.

The constant frequency difference between bands in the visible or in the infra-red which one might expect from Baly's theory have not been found. This detailed discussion of the results has been undertaken to see if the theory does account for the position of the visible absorption

¹ Chem. Soc. of Lon. Trans., 93, p. 1902, 1908.

² Baly, Astrophys. Jour., 42, p. 44.

bands. The proof may be sufficient. It would however be going too far to say that the results are as conclusive as might be desired. From his theory of fluorescence, Baly has predicted that bands would be found at 3.27μ , 3.86μ , 4.72μ , 6.06μ , and at 8.48μ . Only the 3.27μ band has been found, and this band had already been located by Coblenz.

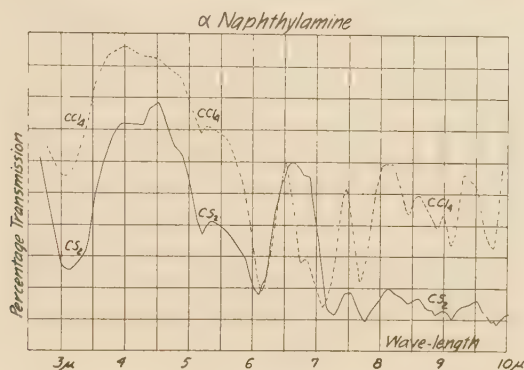


Fig. 13.

TABLE V.

Infra-red Absorption Maxima. Alpha Naphthylamine.

1. No.	2. In CS ₂ .	3.	4. In CCl ₄ .	5.	6. Wave No.	7.
1	3.09 μ ±.04 μ				323	
2			3.18 μ ±.04 μ		314	
3	5.19	.03	5.20	.03	194	N
4	6.10	.03	6.18	.02	163	D
5			6.80	.04	147	
6			7.11	.03	141	
7	7.27	.03			138	ND
8	7.76	.03	7.71	.03	129	D
9	8.44	.03	8.47	.02	118	D
10	8.87	.05	8.92	.03	112	
11	9.11	.02	9.12	.03	110	
12	9.80	.04	9.75	.06	103	ND

Purvis at 3174 (9, 11, 12).

The tables given below for the various isomers list the absorption maxima wave-lengths as found with the two solutions and also show the corresponding wave numbers. In column 7, a band is marked N if it is a naphthalene band, and D if the band is found in both the alpha and the beta derivative. At the bottom of each table is given a list of the wave numbers of the known visible absorption bands and following

each wave number, as before in parenthesis, are the numbers of the infra-red bands which are integral factors of the visible wave numbers. The absorption curves for these compounds are given in Figs. 11 to 15.

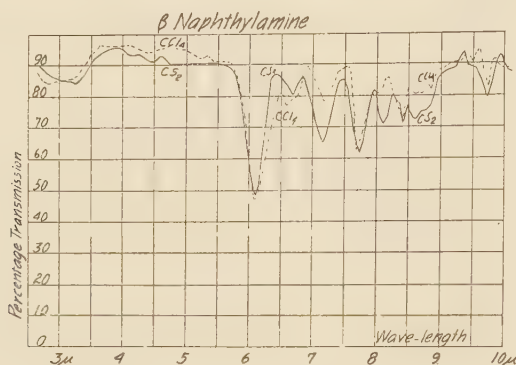


Fig. 14

TABLE VI.

Infra-red Absorption Maxima. Beta Naphthylamine.

1. No.	2. In CS ₂ .	3. In CS ₂ .	4. In CCl ₄ .	5. In CCl ₄ .	6. Wave No.	7.
1			2.86 μ $\pm$.04 μ		350	
2	3.25 μ $\pm$.02 μ				308	N
3	4.44 .04		4.44 .04		225	
4	6.13 .03		6.13 .02		163	D
5	6.67 .03		6.64 .04		150	
6	7.18 .03		7.20 .02		139	ND
7	7.73 .02		7.74 .03		129	D
8	8.09 .02				124	
9	8.40 .03		8.41 .02		119	D
10	8.59 .03				116	
11	9.74 .03		9.76 .02		103	ND

Purvis at 2922 (3, 4, 6, 10) and 3470 (5, 6, 9).

CONCLUSIONS.

1. The absorption of naphthalene and of several of its derivatives has been investigated from 2.7 μ to 10 μ in solutions of carbon disulphide and carbon tetrachloride.

2. Bands which are present when one of the solvents is used are nearly always present or indicated by breaks in the curve when the other solvent is used.

3. Although the positions of maximum absorption are generally the

¹ Purvis, Chem. Soc. of Lon. Trans., 101, p. 1315, 1912.

same, in both solutions, the general appearance of the absorption curves may be very different.

4. Naphthalene has several absorption bands which are due to the benzene nucleus.

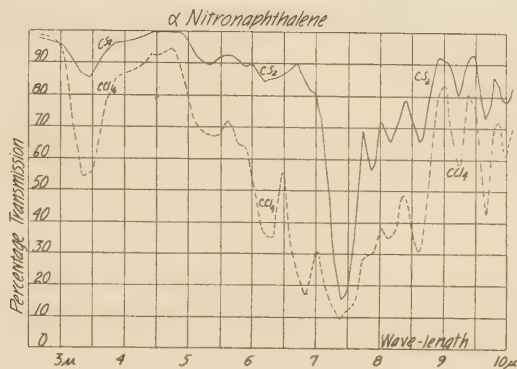


Fig. 15.

TABLE VII.

Infra-red Absorption Maxima. Alpha Nitronaphthalene.

1.	2.	3.	4.	5.	6.	7.
No.	In CS ₂ .		In CCl ₄ .		Wave No.	
1	3.44 μ $\pm$.02 μ		3.42 μ $\pm$.02 μ		282	
2	5.29	.04	5.36	.04	188	
3	6.22	.04	6.24	.03	160	
4			6.83	.02	146	N
5	7.42	.02	7.42	.03	135	
6	7.87	.02			127	N
7	8.17	.03	8.20	.04	122	N
8	8.67	.03	8.62	.03	116	
9	9.25	.02	9.23	.03	108	
10	9.67	.02	9.66	.03	103	
11	9.95	.03	9.96	.03	101	

Purvis at 2930 (4, 6, 7, 9, 11).

5. The mono-derivatives of naphthalene have several of the naphthalene absorption bands.

6. There are however many absorption bands present which are characteristic of the derivative itself.

7. Those naphthalene bands occurring in the alpha derivative are generally present in the beta derivative and there are always several other bands common to both derivatives.

8. The infra-red absorption curve of the alpha derivative is however as a whole different from that of the beta derivative in the same solvent.

9. Nearly all wave numbers of absorption bands for these substances in the visible possess, as integral factors, two or more infra-red absorption maxima wave numbers as Baly's theory predicts.

In conclusion, the writer desires to thank Professor H. M. Randall for proposing the subject and also for many valuable suggestions during the progress of the work.

PHYSICAL LABORATORY,
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May 2, 1916.

OSCILLATORY SPARK DISCHARGES BETWEEN UNLIKE METALS.

BY D. L. RICH.

INTRODUCTION.

IT is known by physicists that there are some twenty factors affecting the production of an oscillatory spark discharge; furthermore, with a few exceptions, there is general agreement as to the part each one of these factors plays. One of the exceptions noted is the effect of the electrode material itself, and that particular phase of the subject forms the basis of this paper.

In view of the very great amount of work that has been done in connection with the electric spark, the effect of the electrode material is very rarely mentioned. In practically all research work on spark discharges the spark has been formed between electrodes of like material, so that opportunities for observing the effect of dissimilar materials have been in general absent. Considering the extensive literature on the oscillatory spark discharge, the lack of experimental data for sparks between electrodes of unlike material is surprising. On the other hand, the effect of the electrode material on the electric arc, both D.C. and A.C., and the behavior of what are known as crystal rectifiers, have been subjects of wide investigation in recent years, and the well-known results therein determined would naturally lead one to believe that the electrode material is not a negligible factor in any electric discharge.

PREVIOUS WORK ON THIS PROBLEM.

One of the earliest investigators of the effect of the electrode material was Righi.¹ He found no difference in the sparking potential in the case of C, Bi, Zn, Sn, Pb and Cu. In 1878, De La Rue and Müller,² in addition to their work on the effect of the shape of the electrodes, used their 10,000-cell silver chloride battery to produce sparks between similarly shaped electrodes of unlike material, Cu, Ag, Pt, Mg, Zn, Al, brass and steel. They also found no difference, except in the case of aluminum, from which sparks could be drawn apparently a little more easily. In 1892, Peace³

¹ Righi, *Nuovo Cimento*, 16, p. 97, 1876.

² De La Rue and Muller, *Phil. Trans.*, Part 1, p. 55, 1878.

³ Peace, *Proc. Soc. Lond.*, 52, p. 109, 1892.

worked with Cu, Zn and brass electrodes. His method was to apply a storage battery to two spark gaps connected in parallel. These spark gaps were set at unequal lengths, and enclosed in separate receivers from which the air could be exhausted; then by changing the gas pressure the sparks were shifted from one gap to the other. No variation produced by interchanging the electrode materials was observed. In 1903, Carr¹ measured the breakdown potential difference for brass, Fe, Zn and Al. He likewise found no difference.

When the spark gap is exceedingly short, as in the case of the coherer, the material undoubtedly affects the discharge. Guthe² was the first to point this out, showing in 1901 that the cohering effect between electrodes of unlike material takes place at a lower voltage in one direction than in the reverse direction. Hobbs,³ using like electrodes and very short spark-lengths (two to six wave-lengths of light) claims that the metallic ions take part in the discharge, with the result that the material of which the electrode is composed exerts an important influence on the spark potential. Almy⁴ attempts to connect cathode fall with spark potential. To quote him, "The fact that different metals show marked difference in the so-called cathode fall obviously leads to the inference that spark potentials must to a certain extent depend on the material of the electrode used." Later he says, "In air the cathode fall of the different metals differs so little that it hardly seemed probable a difference in spark potentials would be detected." His experimental work was done almost entirely with hydrogen as the gas in which the electrodes were immersed. He used a storage battery to furnish the voltage, and a Weston voltmeter to measure it. In hydrogen he finds fairly consistent differences due solely to the material of the electrodes. In air the only variation in sparking potential that he mentions is in the case of Pt-Al electrodes, the Pt-Al⁺ discharge requiring eight volts more than the Pt⁺Al⁻ discharge.

The work of Schuster and Hemsalech,⁵ followed by that of Milner⁶ and of Royds,⁷ throws much light on the behavior of metallic ions in the spark gap. These men photographed the spark on a rapidly revolving film, allowing the light to pass through a spectroscope placed between the spark gap and the film. The appearance of the photographed lines enabled

¹ Carr, *Phil. Trans.*, A, 201, p. 419, 1903.

² Guthe, *Annalen der Physik*, 4, p. 762, 1901.

³ Hobbs, *Phil. Mag.*, 10, p. 619, 1905.

⁴ Almy, *Univ. of Nebraska Studies*, Vol. 6, No. 4, 1910.

⁵ Schuster and Hemsalech, *Phil. Trans.*, A, 193, p. 189, 1899.

⁶ Milner, *Phil. Trans.*, A, 209, p. 71, 1909.

⁷ Royds, *Phil. Mag.*, 19, p. 285, 1910.



Fig. 1.



Fig. 2.



Fig. 3.

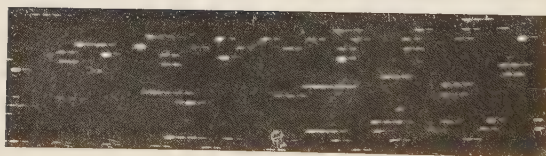


Fig. 5.

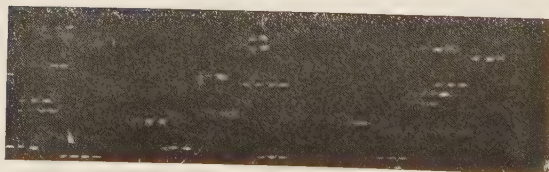


Fig. 6.

D. L. RICH.

them not only to identify the metallic vapors present in the spark, but also to compute the velocities with which these vapors traveled out into the spark gap from each electrode. Their results show that the different metal vapors travel with unequal velocities. Since their work was mainly the determination of ionic velocities they were not concerned with the critical sparking potential, nor with rectification effects. It is however only a logical probability that if the metal ions travel with unequal velocities these same ions are liberated from the electrodes with unequal facility, and therefore the spark might start more readily from some metals than from others; in other words, the measurements of Schuster and Hemsalech rather support the idea that rectification effects due to electrode material do exist.

THE PROBLEM.

If there is a rectification effect of this nature, it should manifest itself when an alternating electromotive force of sufficient magnitude is applied to unlike electrodes. And the behavior of the spark discharge is probably best studied by photographing the spark gap while the discharge is taking place.

Our problem then is really this: *Apply an alternating electromotive force to an oscillatory circuit containing a spark gap made of electrodes mechanically alike but chemically different and determine by photographing the spark whether or not the oscillatory discharge starts as readily when one electrode is anode as when the other is anode.* During one of the series of half-cycles, say that series consisting of the first, third, fifth, seventh, etc., half-cycles, one of the electrodes will be initially an anode; while in the other alternate series, consisting of the second, fourth, sixth, etc., half-cycles, this same electrode will be initially the cathode.

To photograph the spark gap in air at ordinary atmospheric pressure, three principal methods are available: (a) To insert either a rotating mirror or a rotating lens between the spark gap and the stationary sensitized surface of the camera. Feddersen, and Trowbridge, for example, used the rotating mirror, while Boyd used a series of rotating lenses. (b) To separate the otherwise superimposed oscillations by blowing the sparks from the narrow to the wide end of a V-shaped spark gap by means of a powerful blast of air. Klingelfuss was the first to use this method. (c) To receive the image of the spark on a rapidly revolving plate or film. Pierce, and Lodge and Glazebrook used a revolving plate, while Schuster and Hemsalech used a revolving film.

The second method was discarded as undesirable, and throughout this work there has been used a combination of the first and the third methods

outlined above, the photographic lens being moved with rather slow velocity, and the photographic film or plate with a much higher velocity.

FIRST METHOD USED—PLATE CAMERA.

In order to observe the relative number of spark trains per half-cycle no excessive speed of the photographic surface is necessary. For this the following method was found satisfactory. An ordinary glass plate negative, held in its customary plate holder which in turn was clamped centrally on the end of the shaft of a small motor, and at right angles to the shaft, so that the plate could be turned at a fairly high speed in its own plane, was the arrangement used for moving the photographic surface. In order to prevent the superposition of images the lens of the camera was swung slowly across in front of the plate and parallel to it, so that the successive spark trains traced out a spiral on the plate.

To produce these sparks a spark gap, an inductive resistance, and a condenser were connected in series, and then the condenser put directly across the secondary of a rather leaky high voltage transformer whose primary was connected to 110-volt 60-cycle mains.

Figs. 1, 2 and 3 are reproductions of photos secured in this way. Each spot represents not a single spark but a complete train of sparks, the speed of rotation not being sufficiently great to separate the individual oscillations. The groups of spark trains correspond to the half-cycles of the exciting primary current. The asymmetry of the spark trains per half-cycle is very plainly evident, every second half-cycle containing many trains, and the alternate half-cycles fewer trains. In Fig. 1 is a half-cycle (marked "o") that produced no spark trains whatsoever. In Fig. 2 several alternate half-cycles trail off into a tail, indicating that the oscillatory discharge degenerated into an ordinary arc discharge. To test this, the capacity and the inductance were disconnected, and Fig. 3 is the appearance of the resulting arc.

INTERPRETATION AND PREDICTIONS.

Figs. 1, 2 and 3 are photographs taken when the electrode materials were copper and iron. The asymmetry of the spark trains per half-cycle indicates that there is a rectification effect present in the oscillatory discharge between two electrodes of dissimilar material. Probably if the critical voltage were secured (a difficult task, but not impossible) spark trains would be produced only on alternate half-cycles, the others being entirely suppressed. Even if this critical voltage were not used, but instead a voltage somewhat higher than the critical, rectification effects when present would manifest themselves in at least three ways:

1. *In the Relative Number of Spark Trains per Half-cycle.*—If we assume that the sparks start more easily at one electrode than at the other, we are led immediately to the conclusion that the sparks must start more readily on one half-cycle than on another; that one set of alternate half-cycles will produce more spark trains than the other alternate set. The following diagram (Fig. 4), it is reasonable to suppose, might represent what our assumption leads us to expect. Suppose the electrodes are Cu and Fe, and that the first half-cycle occurs when Fe is initially positive, and the second half-cycle when the electrode Fe is initially negative; and suppose further that we assume that the spark starts the more readily

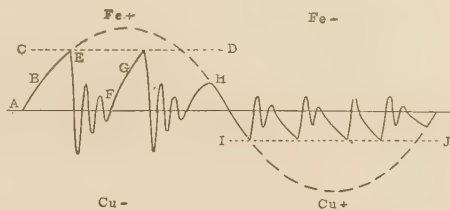


Fig. 4.

when Fe is negative than it does when Cu is negative. This amounts to the same as assuming that the sparking potential, or the difference of potential necessary to initiate a spark, is relatively high on the Cu-Fe^+ half-cycles and relatively low on the Cu^+Fe^- half-cycles. The potential builds up along the curve AB until it reaches the sparking potential CD at the point E . Then a discharge takes place, either unidirectional or oscillatory as the case may be, with the result that the potential difference is reduced to a magnitude less than that necessary to maintain the discharge (not necessarily reduced to zero, however). The voltage then builds up again, let us say along some such line as FG , and the process repeats itself until finally the curve reaches H and no further discharge takes place until the potential difference builds up in the opposite sense in the next half-cycle, with Fe initially negative. Owing to the relatively high potential necessary to initiate a spark, only a relatively small number of trains will be produced in this Cu-Fe^+ half-cycle.

During the next half-cycle, if the sparking potential IJ is small, the discharges will have a chance to begin *earlier* in the half-cycle; after the falling off of the potential due to the discharge, the potential can build up again to the necessary sparking magnitude *more quickly*; and the sparks can start and last *later* in the half-cycle; *all three* of these factors tend to produce *more discharges* in this Cu^+Fe^- half-cycle than in the preceding Cu-Fe^+ half-cycle.

2. *In the Relative Number of Individual Oscillation Sparks per Train.*—When a spark does occur at the higher sparking potential, this spark might reasonably be expected to be of a more violent nature than a spark produced at a lower sparking potential. If more violent, not only would

the condenser be more strongly charged in the opposite sense, but there would also be more ions produced in the spark gap, with the result that the spark gap resistance would be decreased. Both the stronger charge and the lowered resistance would lead one to expect that the oscillations following the initial spark would be more numerous. The large initial charge and the smaller damping decrement would each tend to prolong the duration of the wave train.

3. *In the Relative Number of Spark Trains Containing an Even Number, or an Odd Number, of Individual Oscillation Sparks.*—So far as the material affects matters, if the initial spark in any train starts with ease, the third, fifth, etc. (the *odd* sparks), in that same train, since they start from the same electrode, should also start with ease, with greater ease than the second, fourth, etc. (the *even* sparks), which originate at the other electrode, from which the spark starts with difficulty. It would naturally be expected that any spark train would stop with an easy spark, *i. e.*, at the beginning of a spark difficult to start. That is, if the initial spark of any train starts easily, that particular spark train might be expected to contain an *odd* number of sparks. Likewise, the train whose first spark originates at an electrode from which the spark starts with difficulty should in general contain an *even* number of individual sparks.

But in addition to the material of the electrodes there are at least two other factors (even with the electrodes mechanically and chemically alike) that probably have an influence on the oddness or evenness of the number of sparks per train. The primary current is changing while the secondary discharge is taking place. The flux change in the secondary due to this slowly changing low frequency primary current, combined with the flux change in the secondary due to the rapidly changing high frequency secondary current, since these two changes are in the same sense during half the sparks and in opposite sense during the other half, would probably produce an asymmetry that would favor one set of sparks always whether the electrodes were of the same material or not.

Also, the ionization produced in the spark gap is a function of the velocity of the ions, which velocity is in turn dependent on the potential at which the ions were emitted,—a high potential difference producing a high velocity and therefore a low capacity for ionization. So considering the three factors, and not knowing their relative magnitudes it is impossible to predict which spark trains will contain an even number of individual oscillation sparks, and which an odd number.

REASONS FOR CHANGING TO A FILM CAMERA.

To investigate the above matters it became necessary to rearrange both the camera and the oscillatory circuit. The first method used, and

the photographs secured, samples of which are shown above, are satisfactory to determine the relative number of spark trains per half-cycle; but to obtain photographs showing individual oscillation sparks the photographic surface must be made to move at a very much higher rate, and the period of the oscillatory discharge must be lengthened to secure a much lower frequency.

To lower the frequency a larger inductance coil and a larger condenser were built. The inductive resistance was a circular coil a meter in diameter and a meter high, and consisted of about a hundred turns of no. 12 coppered iron wire wound on a rough wooden frame. Its low frequency resistance was 6.5 ohms, and its low frequency inductance 25 millihenrys. The condenser was made of 48 large panes of ordinary window glass, each pane shellacked, coated on both sides to within five centimeters of the edge with tin foil, then given two more coats of shellac. The panes were mounted in a wooden frame with air insulation. When thoroughly dry the leakage was not excessive, but the absorption was very bad. The low frequency capacity ranged from an eighth to a half microfarad, depending on the duration of the charge and of the discharge.

To increase the speed of the camera the glass plate was abandoned and a film used instead (Eastman extra rapid speed film, about 55 inches long and $2\frac{1}{2}$ inches wide). The film was wrapped around the flat outside rim of a wheel 40 cm. in diameter. This made the total exposed length of the film about 1,260 mm. The wheel was mounted on a motor running 2,000 revolutions per minute, giving a linear velocity to the film of about 42,000 mm. per second. In order to hold the film in position at this rather high speed it was found necessary to bolt the film to the wheel with twelve bolts arranged zigzag around the circumference. By actual measurement of the developed films it was found that this inductance, capacity and film speed resulted in a separation of the individual oscillation sparks to distance of 4.1 mm., a distance amply sufficient for all present purposes.

As before, exposure was made by swinging the lens across the film while the film was rotating at a high speed, so that the spots of light traced out a continuous spiral on the film. The lens was moved by a heavy weight which in falling from ceiling to floor picked up counterbalancing weights so that its speed was kept approximately constant. Further the weight in falling automatically operated a mercury switch so that the spark discharge took place only while the lens was passing in front of the film. By adjustment it was found possible to cause the spiral to trace out twenty complete turns on each film, thus *enabling the spark gap to be kept under continuous observation for over half a second at a time*,

showing the groups of spark trains in over sixty consecutive half-cycles all spread out in a single line photograph over twenty-five thousand millimeters long.

Data Secured from a Typical CuFe Photo.

Half-cycles in Which Fe Was Initially Negative.				Half-cycles in Which Fe Was Initially Positive.			
Half- cycle.	Num- ber of Spark Trains.	Number of Sparks in Each Train.	Total Num- ber of Sparks.	Half- cycle.	Num- ber of Spark Trains.	Number of Sparks in Each Train.	Total Num- ber of Sparks.
1		Incomplete		2		Incomplete	
3		Incomplete		4		Incomplete	
5	4	5 2 2 2	11	6	3	5 3 3	11
7	7	4 2 2 2 2 2 2	16	8	2	5 3	8
9	2	5 3	8	10	4	4 2 3 3	12
11	6	4 2 2 2 2 2	14	12	2	5 3	8
13	6	4 2 2 2 2 2	14	14	2	5 3	8
15	5	4 2 2 2 3	13	16	3	4 3 3	10
17	5	5 2 2 2 3	14	18	3	5 3 3	11
19	9	4 2 2 2 2 2 2 2 2	20	20	2	5 3	8
21	8	4 2 2 2 2 2 2 2	18	22	4	5 3 3 3	14
23	7	4 2 2 2 2 2 2	16	24	3	5 3 3	11
25	5	4 2 2 2 2	12	26	3	4 3 3	10
27	5	4 1 2 3 2	12	28	3	4 3 3	10
29	4	4 3 2 3	12	30	3	4 3 3	10
31	8	4 2 2 2 2 2 2 2	18	32	4	4 3 2 3	12
33	6	4 2 2 2 2 2	14	34	3	5 3 3	11
35	9	4 2 2 2 2 2 2 2 2	20	36	2	5 3	8
37	8	4 2 2 2 2 2 2 2	18	38	3	5 3 3	11
39	7	4 2 2 2 2 2 2	16	40	3	3 3 3	9
41	5	3 3 2 2 2	12	42	5	3 2 2 2 3	12
43	9	4 2 2 2 2 2 2 2 2	20	44	2	3 3	6
45	7	4 1 2 2 2 2 2	15	46	4	3 3 3 3	12
47	7	3 2 2 2 2 2 2	15	48	3	3 3 3	9
49	7	4 2 2 2 2 2 2	16	50	4	3 3 3 3	12
51	7	4 2 2 2 2 2 2	16	52	2	5 3	8
53	9	4 2 2 2 2 2 2 2 2	20	54	4	4 2 2 3	11
55	8	4 2 2 1 2 2 2 2	17	56	3	3 3 3	9
57	8	4 2 2 2 2 2 2 2	18	58	4	4 2 2 3	11
59	11	2 2 2 2 2 2 2 2 2 2 2	22	60	3	3 3 3	9
61	8	3 2 2 2 2 2 2 2	17	62	4	3 3 3 3	12
63	8	4 2 2 2 2 2 2 2	18	64	4	3 3 3 4	13
65		Incomplete		66	4	3 3 3 3	12
67		Incomplete		68	3	3 3 3	9

To show relative number of spark trains per half-cycle, and also to show relative number of oscillation sparks per train, it is desirable to use a short spark gap, and highly damped oscillations. Fortunately these conditions are the very easiest possible.

A large number of photographs were taken, in an interval extending over two years. Most of the work was done on CuCu and CuFe electrodes in an attempt to settle definitely the point in question with these particular metals. Later electrodes of zinc and bismuth were used in various combinations with each other and with copper and iron. Many different specimens were used, and several different shapes. The sparks were always produced in air at atmospheric pressure. The spark gap was varied in length from 0.1 mm. to 3 or 4 mm., while the lens of the camera was so placed that the image of the spark gap was slightly longer than the spark gap itself.

Figs. 5 and 6 are sections of typical films showing the appearance of the sparks between CuFe electrodes and CuCu electrodes respectively. Owing to the fact that some of the beginning and the ending half-cycles are incomplete on the edges of the films, the number of half-cycles observable in the two series are in general unequal; however, no error is thus introduced as average values are desired, and any number of half-cycles may be averaged.

CuFe Summary.

	Cu ⁺ Fe ⁻ .	Cu ⁻ Fe ⁺ .
Total number of half-cycles observed.....	30	32
Total number of spark trains.....	205	101
Average number of spark trains per half-cycle.....	6.2	3.16
Total number of oscillation sparks.....	472	327
Average number of oscillation sparks per train.....	2.3	3.23
Number of trains consisting of 1 spark.....	3	0
Number of trains consisting of 2 sparks.....	166	9
Number of trains consisting of 3 sparks.....	10	71
Number of trains consisting of 4 sparks.....	23	9
Number of trains consisting of 5 sparks.....	3	12
Total number of spark trains consisting of an <i>even</i> number of sparks.....	189	18
Total number of trains consisting of an <i>odd</i> number of sparks.....	16	83
Per cent. even.....	92.2	17.7
Per cent. odd.....	7.8	82.3

An examination of the CuFe data summary shows that the spark trains on the Cu⁺Fe⁻ half-cycles were almost double the number of trains on the Cu⁻Fe⁺ half-cycles (6.2 to 3.16); that the number of oscillation sparks per train was over a third larger (2.3 to 3.23) in the Cu⁻Fe⁺ half-cycles than in the Cu⁺Fe⁻ half-cycles; and that in the Cu⁻Fe⁺ half-cycles 82 per cent. of the trains contained an *odd* number of sparks, while in the Cu⁺Fe⁻ half-cycles 92 per cent. of the trains contained an *even* number of sparks.

INTERPRETATION.

The relative number of spark trains per half-cycle, and the relative number of sparks per train indicate clearly that the Cu^+Fe^- discharge takes place more readily than the Cu^-Fe^+ discharge. The fact that an odd number of sparks per train predominates during the Cu^-Fe^+ half-cycles and an even number during the Cu^+Fe^- half-cycles indicates that the ionizing effect is the predominating influence in determining the evenness or oddness, as the sparks as a rule stop with the higher voltage, higher velocity, lower ionizing discharge.

In contrast with the preceding data, which was secured from a typical series of discharges between electrodes mechanically alike but chemically different, and which show rectification effects attributable solely to electrode material, compare the following set of data, from a characteristic series of discharges between CuCu electrodes.

Summary of Data Secured from a Typical CuCu Photo.

	Odd Half-cycles.	Even Half-cycles.
Total number of half-cycles observed.....	31	33
Total number of spark trains.....	63	74
Average number of spark trains per half-cycle.....	2.03	2.24
Total number of oscillation sparks.....	250	291
Average number of oscillation sparks per train.....	3.97	3.93
Number of trains consisting of 1 spark.....	0	0
Number of trains consisting of 2 sparks.....	0	0
Number of trains consisting of 3 sparks.....	10	7
Number of trains consisting of 4 sparks.....	45	64
Number of trains consisting of 5 sparks.....	8	3
Number of trains consisting of an <i>even</i> number of sparks.	45	64
Number of trains consisting of an <i>odd</i> number of sparks.	18	10
Per cent. even.....	71.5	86.5
Per cent. odd.....	28.5	13.5

An examination of the CuCu data summary preceding shows that the average number of spark trains per half-cycle is practically the same in the two series (2.03 to 2.24); that the average number of individual sparks per train is almost identically the same (3.97 to 3.93); and that in both series the spark trains are predominantly of four sparks each. In not one of these three respects is there even any hint of rectification effects. The irregularities which do occur in discharges of this nature are probably due to the conducting variations in the spark gap, possibly caused by air-currents, etc., variations which prevent the absolutely uniform charging of the condenser.

In every photograph, without a single exception, I have found the CuCu discharge to be symmetrical, and the Cu^+Fe^- discharge to be more easily produced than the Cu^-Fe^+ discharge.

DETERMINATION OF POLARITY.

In order to determine which particular kind of spark should be associated with the Cu-Fe^+ discharge, and which with the Cu^+Fe^- , the A.C. primary circuit was disconnected and there was substituted a 220-volt D.C. source, through a suitable non-inductive high resistance and a knife switch. The fact that the primary E.M.F. was high, produced a rapid change of flux in the transformer when the switch was closed, and consequently a vivid spark in the secondary circuit; yet the resistance inserted in the primary circuit resulted in less than a volt across the primary coils, so that it was perfectly safe to put an ordinary 250-volt voltmeter directly across the secondary of the high potential transformer, and thus determine definitely and easily the polarity of the spark electrodes at make and at break. The voltmeter behaved as a ballistic galvanometer, and by the direction of its "kick" gave positive evidence concerning the polarity.

The camera film was set in motion, the camera shutter closed except at "make," and a series of make spark photos secured. Then the lens was displaced sideways slightly, the shutter closed except at "break," and a series of break spark photos obtained. The electrodes were then reversed, and the make and the break photos again taken, all on the same film, side by side.

When the primary circuit was closed, a single spark train was expected. As a matter of fact the photographs showed several spark trains for each make, the number varying from four to forty-two, depending on the length of the spark gap. This may be explained as follows:

Suppose the total quantity of electricity flowing into the condenser of the secondary circuit be plotted against time, giving the familiar curve of Fig. 7. A quantity q_1 might be sufficient to charge the condenser to

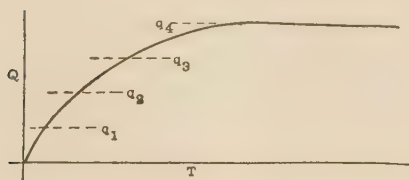


Fig. 7.

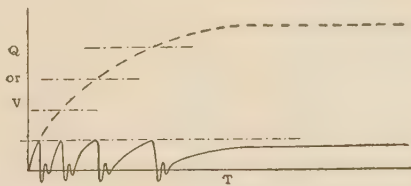


Fig. 8.

the sparking difference of potential, and an oscillatory discharge would then occur. A further quantity $q_2 - q_1$ might again charge the condenser, and another oscillatory discharge ensue; and again a quantity $q_3 - q_2$, and still further $q_4 - q_3$, and so on, might each cause a spark train. The fact that at each make the first spark trains were not only

more intense but also made up of from five to eight oscillation sparks each, while the later spark trains were of less intensity and also of shorter length (2, 3, or 4 oscillation sparks each) supports the above explanation. The curve (Fig. 8) probably represents what took place:

Owing to the arcing effect at the knife switch when the primary circuit was opened, usually only one spark train was observed at "break," and it was usually much fainter than the sparks at "make."

Several films were used in this manner. In every case the photos of the Cu-Fe^+ discharge consisted of light, narrow, faint spots alternating with heavy, broad, darker spots, and *always beginning with the fainter spot*, as shown in (a) Fig. 9; while the Cu^+Fe^- discharge photo was of similar alternations, but *always beginning with the broad dark spot*, as shown in (b), Fig. 9. The metallic vapor liberated in the spark gap when iron was anode always produced the much more intense light effect. On all the photos, whether produced by direct current or alternating current means, the polarity of the electrodes could be identified easily and positively. Furthermore, on the D.C. photos, the Cu^+Fe^- discharge without exception consisted of an even number of oscillation sparks; while the Cu-Fe^+ generally, though not always, consisted of an odd number of sparks.



Fig. 9.

When the electrodes were of the same material, for example CuCu , the sparks were always of like character throughout, gradually growing fainter as the amplitude decreased, as shown in (c), Fig. 9. Furthermore the number of individual oscillation sparks when the electrodes were alike was predominantly even.

FURTHER RESULTS WITH OTHER ELECTRODE COMBINATIONS.

It next seemed desirable to investigate the behavior of some other metals when used as electrodes, in order to see whether or not there exists a consistent rectification series among conductors in general. The same method was continued, and zinc, bismuth, copper and iron electrodes were used repeatedly in all possible combinations.

Iron-bismuth was one of the first combinations tried. Below is a summary secured from a typical Fe-Bi photo.

An examination of this summary, particularly the relative number of spark trains per half-cycle, and the relative number of oscillation sparks per train, indicates that the discharge can start more readily when iron is negative. Each of the other films of this particular electrode combination indicated the same rectification. Not much reliance, however, can be placed on the relative number of even and odd spark trains.

Iron-Bismuth Summary.

	Fe-Bi ⁻ .	Fe ⁺ Bi ⁺ .
Total number of half-cycles observed.....	28	29
Total number of spark trains.....	146	83
Average number of spark trains per half-cycle.....	5.21	2.86
Total number of oscillation sparks.....	218	184
Average number of oscillation sparks per train.....	1.49	2.21
Number of trains consisting of 1 spark.....	76	15
Number of trains consisting of 2 sparks.....	68	35
Number of trains consisting of 3 sparks.....	2	33
Number of trains consisting of an even number of individual sparks.....	68	35
Number of trains consisting of an odd number of individual sparks.....	78	48
Per cent. even.....	46.5	42.1
Per cent. odd.....	53.4	57.8

After finding that the spark discharge could be initiated more readily from iron than from either copper or bismuth (always assuming that the discharge is electronic in nature, so that the current flows from anode to cathode), the next step seemed to be the investigation of the copper-bismuth spark gap. Below is a copy of the data secured from a characteristic CuBi film. Note the 3's.

Copper-Bismuth Summary.

	Cu ⁺ Bi ⁻ .	Cu ⁻ Bi ⁺ .
Total number of half-cycles observed.....	32	32
Total number of spark trains.....	69	34
Average number of spark trains per half-cycle.....	2.16	1.06
Total number of oscillation sparks.....	201	101
Average number of oscillation sparks per train.....	2.91	2.97
Number of half-cycles producing no spark.....	1	5
Number of trains consisting of 1 spark.....	0	0
Number of trains consisting of 2 sparks.....	7	1
Number of trains consisting of 3 sparks.....	61	33
Number of trains consisting of 4 sparks.....	1	0
Number of trains consisting of an even number of individual sparks.....	8	1
Number of trains consisting of an odd number of individual sparks.....	61	33
Per cent. even.....	11.5	3
Per cent. odd.....	88.4	97

Here again, as in all of this work, the criterion as to rectification lies in the relative number of spark trains per half-cycle. After the spark is once started various extraneous and uncontrollable irregularities lessen the reliability that can be placed on the way in which that particular spark train continues. On the above film, twice as many spark trains originated from the bismuth anode as from the copper anode. And five

times as many failures to produce any discharge whatsoever are charged to the copper anode.

Another combination tried was zinc and iron. The spark when iron is anode is always easily recognized, the light from the spark then apparently being exceedingly rich in actinic rays.

<i>Iron-Zinc Summary.</i>		
	Fe-Zn^+	Fe-Zn^-
Total number of half-cycles observed	31	29
Total number of spark trains	96	41
Average number of spark trains per half-cycle	3.1	1.41
Total number of oscillation sparks	181	115
Average number of oscillation sparks per train	1.88	2.80
Number of trains consisting of 1 spark	46	4
Number of trains consisting of 2 sparks	17	1
Number of trains consisting of 3 sparks	31	35
Number of trains consisting of 4 sparks	2	1
Number of trains consisting of 5 sparks	0	0
Number of trains consisting of an even number of individual sparks	19	2
Number of trains consisting of an odd number of individual sparks	77	39
Per cent. even	19.8	4.9
Per cent. odd	80.1	95.0

Here again the half-cycles in which iron was initially the anode produced considerably more than twice as many spark trains as the other series. In fact, the discharge took place so readily from the iron anode that the condenser could receive only a very small quantity of electricity, so small that a return spark was very frequently impossible, as is shown by the fact that 46 of the trains (48 per cent. of them) were unidirectional, one spark discharges.

One of the most prominent cases of rectification which was observed occurred in connection with a copper-zinc spark gap. The data for this particular gap is inserted here not as a typical case, but as a special case, illustrating the fact that with proper adjustment it is possible to initiate spark trains from one electrode alone. The necessary adjustment probably would be difficult to make, and still more difficult to maintain, but the following data show that it can be done.

Other films in the CuZn spark gap, while not so prominently asymmetrical as this one, always showed a decided preponderance of spark trains initiated during the half-cycles when zinc was anode, indicating that a discharge could start from zinc much more readily than from copper.

An inspection of the foregoing summaries shows that rectification effects manifest themselves prominently in the relative number of trains per half-cycle, and generally in the relative number of sparks per train.

Copper-Zinc Summary.

	Cu-Zn^+ .	Cu^+Zn^- .
Total number of half-cycles observed.....	32	30
Total number of spark trains.....	14	143
Average number of spark trains per half-cycle.....	1.27 ¹	4.77
Total number of oscillation sparks.....	38	253
Average number of oscillation sparks per train.....	2.71	1.77
Number of half-cycles producing 0 trains.....	21	0
Number of trains consisting of 1 spark.....	1	55
Number of trains consisting of 2 sparks.....	2	72
Number of trains consisting of 3 sparks.....	11	10
Number of trains consisting of 4 sparks.....	0	6
Number of trains consisting of an even number of individual sparks.....	2	78
Number of trains consisting of an odd number of individual sparks.....	12	65
Per cent. even.....	14.3	54.5
Per cent. odd.....	85.7	45.4

Since other factors enter into the cause of oddness or evenness of the number of sparks per train, not so much reliance can be placed on the relative number of odd and even trains.

As a result of the work discussed in this paper the conclusion is reached that rectification effects do exist in oscillatory discharges between the unlike metals used, the order being Fe, Bi, Zn, Cu, a spark being initiated with the greatest facility from iron, and with the greatest difficulty from copper.

More complete data of this nature, involving the various elements which may be used as electrodes, may throw light on the stability of ionic or electronic aggregations or orbits within the atom.

COMPARISON WITH A FORMER RESULT.

It has already been mentioned that Guthe was the first to suggest that the discharge in the case of the coherer is undoubtedly affected by the material of the electrodes. In an attempt to measure the smallest potential difference necessary to produce coherer action Guthe² experimented with many different metals, among which were the same four, Cu, Bi, Fe and Zn, mentioned in this paper. Since in the coherer the two electrodes are either in actual contact or else separated by an exceedingly thin layer or film, the conditions are somewhat different from the ordinary spark gap. Further, the potential difference applied to the coherer was a very slowly changing, and finally constant, statical, battery potential difference; whereas the voltage used in this work was always a rapidly changing, alternating, transformer potential difference. Nevertheless, if the discharge is electronic, either method should yield some

¹ 11 half-cycles only.

² Guthe, Ann. d. Physik, 4, p. 762, 1901.

information concerning the facility with which electrons are torn from the anode and fired across the spark gap or the coherer film. Guthe arranges the metals in the order Bi, Fe, Zn, Cu, the series beginning with the easiest and ending with the hardest; *i. e.*, ending with the metal requiring the highest potential difference to produce coherer action. His series differs from the series proposed in this paper only in the relative positions of bismuth and iron.

SUMMARY.

Many photographs of the oscillatory spark discharge between electrodes mechanically alike, but chemically different, were taken, in an attempt to determine whether or not the material of the electrode has any influence on the initiation of the discharge.

Electrodes of copper, iron, zinc and bismuth were used; also both alternating currents and intermittent direct currents were used; in producing the required potential differences.

The interpretation of the relative number of spark trains per half-cycle, the relative number of individual oscillation sparks per train, and the relative number of trains containing odd numbers and even numbers of individual sparks, is given, with reasons for such interpretation.

When the electrodes were alike symmetrical discharges were always found.

When the electrodes were of two unlike metals decided rectification effects were always produced, being very pronounced when copper was one of the electrodes, and most prominent when iron was the other electrode. In other words, the material of the electrodes is not a negligible factor in the initiation of a spark discharge.

If the discharge is electronic, the electrons are emitted from iron more easily than from bismuth or zinc, and much more easily than from copper; they are emitted from bismuth more easily than from zinc or copper; and from zinc more easily than from copper. Arranged in a rectification series, these metals stand

Fe, Bi, Zn, Cu.

The rectification effects seemed marked and consistent throughout. Many and various specimens of metals in various shapes were used all in air at ordinary atmospheric pressure.

In conclusion, my thanks are due to Professor K. E. Guthe, under whose helpful supervision this work was done; and also to Professor N. H. Williams for much good advice during the progress of the work.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICHIGAN,
April 1, 1915.

DEMAGNETIZATION OF IRON.

DEMAGNETIZATION OF IRON.

BY ARTHUR WHITMORE SMITH.

THE magnetic state of a piece of iron depends not only upon the field intensity to which it may be subjected at the moment, but also upon the previous magnetic history of the iron. This is especially true when the applied magnetic field intensity is small. In making a magnetic test of a bar or ring of iron to determine either the B - H induction curve or the μ - B permeability curve it is necessary to use some means to destroy the effect of previous magnetization. Usually this is done by the method of reversals, in which the magnetizing current is reversed many times while at the same time it is gradually reduced to zero. An alternating current¹ is often used for this purpose, but when used to demagnetize solid bars it does not produce the desired result, as is shown below. It is more effective² to use a direct current reversed by hand not faster than one cycle per second while it is slowly reduced, and even then it has been found that the iron is not brought to a constant condition until after a few hundred reversals of the same value of the current.

In a former paper³ it is shown that the magnetic flux does not reach its full value until several seconds after the reversal of the magnetizing current. This is due to eddy currents which circulate in the iron in a direction opposite to that of the applied current, and only after sufficient time has elapsed to allow these eddy currents to die away will the effective magnetic field within the iron reach its full value. It is evident, then, that if the magnetizing current is reversed too rapidly there will be very little effect upon a considerable (interior) portion of the iron, and the demagnetization will be less effective than a few reversals made much more slowly.

The object of the present investigation is to determine the effect of various methods of demagnetization on an iron ring. Suppose, for example, that it is desired to find the magnetic induction, B , corresponding to a given (small) magnetic field intensity, H . If the iron has been previously magnetized it will first be necessary to completely demagnetize it. This treatment should be complete enough to wipe out every trace of perma-

¹ See Searle, Jour. Inst. Elec. Eng., Vol. 34, p. 61, 1904.

² See Burrows, Bull. Bureau of Stand., Vol. 4, p. 205, 1908.

³ Smith, PHYS. REV., Vol. 9, p. 419, 1917.

nent or residual magnetization, and leave the iron equally ready to receive the new magnetization in either direction. There are thus two questions to be answered; first, in what state will a given process of demagnetization leave the iron? and second, in what manner will the B - H magnetization curve, or the μ - B permeability curve, be affected by the method used to demagnetize the iron?

Four different methods of demagnetization were tried. In the first alternating current was used. In the second the magnetizing direct current was reduced to zero without reversal and no further demagnetization was attempted. In the third method the iron was carefully and completely carried through a most thorough process of reversals and one that has been considered sufficient to entirely demagnetize the iron. In the fourth process the current was reversed fewer times, but with much longer intervals between successive reversals.

To show the effect, or rather the lack of effect, of alternating current the iron ring was subjected to a 60-cycle alternating current. The initial current was 1.5 amperes, and this was slowly reduced to .02 ampere. The maximum previous magnetization was with 1.5 amperes of direct current, and the maximum of the alternating current should be well above this. If the iron followed this decreasing magnetic field it should have very little magnetism left after this "demagnetization." Whether it is demagnetized or not, the ring being a closed magnetic circuit gives no external evidence of its condition.

The hysteresis curve for this ring is shown in Fig. 1. The maximum value of H , the magnetic field intensity within the iron, was 13.3 gaussses,¹ that is, 13.3 gilberts per centimeter. This corresponds to a current of 1.5 amperes in the primary winding of the ring. The last application of the direct current was + 1.5 amperes and the circuit was then broken, leaving the iron at E , Fig. 1, just before using the alternating current. Afterwards the same value of the direct current was applied in the reverse direction. Had there been no intermediate treatment this reverse field would have carried the iron from E to D , thus completing half of the hysteresis cycle. The actual deflection of the galvanometer was 109, instead of 119, showing that the alternating current did have a little effect and had reduced the average residual magnetization from OE to OR , Fig. 1. This means that three fourths of the residual magnetization was not removed by the alternating current.

No larger current was used at this time, but after all of the other measurements mentioned in this paper had been completed and the ring

¹ This word is used in accordance with the recommendation of the International Electrical Congress, Paris, 1900. See *The Electrician* (London), Vol. 45, p. 822, 1900. Searle, *Jour. Inst. Elec. Eng.*, Vol. 34, p. 56, 1904. Wolff, *Bull. Bureau of Stand.*, Vol. 1, p. 49, 1904.

had been demagnetized several times by direct current reversals, the alternating current was tried again. Demagnetization by gradually reducing the alternating current from 1.5 amperes to zero, after the iron had been subjected to a direct current of 1.5 amperes, gave practically the same result as before. When the iron was magnetized in the opposite direction the alternating current removed the same fraction of the residual magnetization. This was not the case when the alternating current was reduced by withdrawing a pointed copper electrode from a jar of water in which was a larger fixed electrode. This arrangement caused a partial

rectification of the current and gave it a greater demagnetizing effect in one direction than in the opposite. When the current was reduced by metallic resistances no asymmetry was detected.

Somewhat better demagnetization was obtained by using larger currents. The largest current used was 16 amperes, which would correspond to a maximum field of 200 gauss within the solenoid without the iron. After magnetizing the iron to *D*, Fig. 1, with a direct field of 13.3 gauss this large alternating current, gradually reduced to zero, brought the iron to *Z*, Fig. 1, and left it with a residual magnetization of 4,000 maxwells per square centimeter. Computation shows that about ten times this current would be required to com-

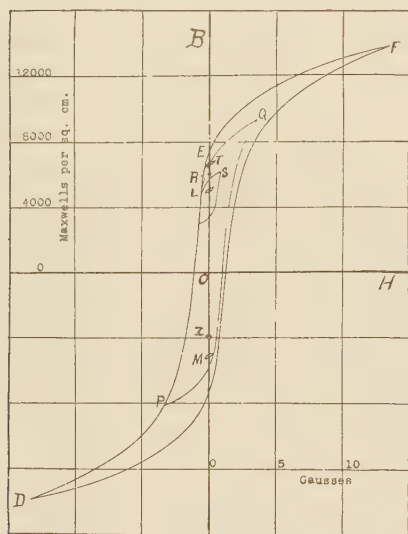


Fig. 1.

Hysteresis curves for a ring of Swedish iron. Demagnetization by alternating current leaves the iron at *R*. At one cycle per second the iron is left at *L*.

pletely demagnetize the iron, but the copper wire used for the magnetizing solenoid would not carry so large a current and it was not tried.

As is shown later, see Fig. 2, if it were assumed that the iron was completely demagnetized, and a *B-H* curve is determined by the usual method of reversals the measured values of *B* will be too small and the resulting curve is not the normal magnetization curve.¹ Moreover, there would be nothing to indicate that the curve does not truly represent the iron of the ring, or that the iron was not properly demagnetized at the beginning.

When the magnetizing field is reduced from its maximum value to zero

¹ See, also, Burrows, Bull. Bureau of Stand., Vol. 4, p. 220, Figs. 4 and 5.

without reversal the iron is brought to E , Fig. 1. This would not be considered as demagnetization at all, but this point is only a little higher than R , where the iron was left by the alternating current.

In the third method the iron ring was demagnetized by using direct current reversed by hand with a mercury commutator at the rate of one cycle per second. At the same time the current was slowly reduced from 1.5 amperes to .05 ampere. Reversing this small current gave a deflection of 2 scale divisions for the total height of the small hysteresis curve. Applying the full reverse current of -1.5 amperes, thus carrying the iron from the lower tip of the small hysteresis curve, L , Fig. 1, to the lower tip, D , of the large hysteresis curve, gave a deflection of 103 divisions. This means that the center of the small curve L is at $B = 5,000$, and thus this demagnetization has left two thirds of the residual magnetization undisturbed.

In the above case the current remained at $+1.5$ amperes for a few minutes before the reversals began. The same process was repeated, but the current was allowed to stand reversed at -1.5 amperes for a short time before beginning reversals. The current was slowly reduced, as before, and the small hysteresis loop for the last reversal of .05 ampere is shown at M . Thus the iron may be left at L or M , depending upon the trivial (?) incident of which way the current was flowing when reversals began.

Of course this is readily explained in the light of the former paper¹ on the time lag of magnetization. Owing to eddy currents in the body of the iron the interior parts are shielded from the effects of the applied current changing at the rate of one cycle per second.

It therefore seems logical to try the demagnetizing effect of a current reversed as slowly as once in ten seconds. The magnetizing current was reduced by twelve steps of such magnitudes as to reduce the induction by approximately equal amounts. At each step the current was reversed once in ten seconds for ten times. Finally the full current was applied, and the iron was found to have been very near to the point O , Fig. 1. Upon repeating this several times there seemed to be a slight effect in favor of the direction of the initial current. The number of reversals at each step was then increased to eleven, which meant that the current was reduced first while H was negative, next when H was positive, then when H was negative, and so on. This left the last small hysteresis loop symmetrical about O . With only three reversals at each step the demagnetization was very satisfactory, and with one reversal at each step the demagnetization was more nearly complete than in any case where the current was reversed as often as once a second.

¹ Smith, PHYS. REV., Vol. 9, p. 419, 1917.

The mere fact that the iron is at O is not sufficient proof that it is in the neutral condition. But if it is not at O it is certain that the iron is not demagnetized. And if the iron has been brought to O by many reversals of the current it should also be in the neutral state.

The particular times mentioned here apply to the particular ring employed, which had a cross section of 4.9 sq. cm. of iron. When using iron of greater section the time effect is proportionately increased, and the current should be reversed more slowly. With iron of smaller section the same demagnetizing effect can be obtained when the current is reversed more rapidly.

In view of the fact that the process of demagnetization by reversing the current as often as once a second does not actually leave the iron in a demagnetized condition, the question arises, what sort of a B - H curve would be obtained by the usual method of reversals? And how would this curve differ from the B - H curve obtained after the ring has been completely demagnetized?

In the first place it may be noted that the reversal of the smallest current carries the iron around the small hysteresis loop L , Fig. 1, instead of the corresponding hysteresis loop at the origin. While the abscissæ of these two loops are the same, the loop at L is less inclined to the H -axis, and therefore the galvanometer deflections will not be the same in the two cases.

Had the magnetic field been simply reduced to zero from its maximum previous value, and then carried through the same cycle of values, the hysteresis loop for the iron would have been at T , and the galvanometer deflection would be still different. From the deflection alone it is not possible to determine which of these three states is being measured. Some information, however, may be obtained by applying the full value of H , thus carrying the iron from the state in question to D . The corresponding change in B is measured by the galvanometer.

If the iron, after being carried around the loop T , is subjected to a slightly larger value of H , and again carried around the hysteresis cycle, the new loop S will be somewhat below T , but it will be as high as possible and still lie within the larger loop FD , and no amount of reversing the current will bring it to O . Larger loops will extend below O as shown by PQ . These loops were experimentally determined for this ring. The final loop will be FD , and this is the only one which is symmetrical about O .

When the iron has been completely demagnetized and then carried through a similar set of magnetizing cycles, starting with the iron at O instead of at T , all of the loops are symmetrical with respect to O , and the last loop is FD .

To find the effect that the method of demagnetization has upon the magnetization curves, these curves were obtained following three different methods of demagnetization. In the first the current was reversed at one cycle per second while at the same time it was slowly and gradually reduced from $H = 60$ gauss, which was the highest field the iron had experienced up to this time. The smallest current was then reversed and the corresponding induction change measured by the fluxmeter-galvanometer which has been previously described.¹ Then the next largest current was used, and so on until the maximum current was reached. The results, expressed in terms of the μ - B permeability curve, are shown by Curve I., Fig. 2.

Again, the iron was magnetized to $H=60$, and the circuit broken. This leaves the iron at a point corresponding to E , Fig. 1. For the sake of comparison the same set of measurements was repeated without any further demagnetization of the iron. The results, expressed in the same way as before, are shown by Curve II., Fig. 2, which, as would be expected, lies below curve I.

Finally, the iron was subjected to a complete demagnetization by reversing the current once in ten seconds while the current was reduced a little after each third reversal. Of course this process was long and slow. The induction measurements were made in the same manner as for the two previous cases, and the results are shown by Curve III., Fig. 2. This indicates a higher permeability than Curve I. In fact, there is more difference between this slow reversal of the magnetizing current and one cycle per second than between the latter and merely reducing the current from its maximum value to zero without reversal.

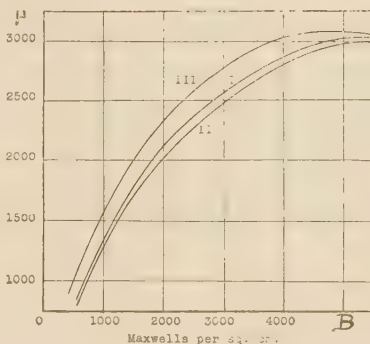


Fig. 2.

Permeability curves. I. After reducing the magnetizing field from $H = 60$ to $H=0$ by many reversals at one cycle per second. II. After breaking the magnetizing current from $H = 90$. III. After demagnetization by reversals once in ten seconds.

CONCLUSIONS.

The proper magnetization curve for a given sample of iron is not obtained unless the iron has been completely demagnetized. Reversals of the magnetizing current at the rate of once a second may be too rapid for effective demagnetization.

¹ PHYS. REV., Vol. 9, p. 415.

When preparing to demagnetize a ring of iron, or other magnetic circuit, the time required for the magnetic flux to become fully reversed should be determined. This is readily done by closing the galvanometer key after the reversal of the magnetizing current and noting what interval, t , is necessary in order that there shall be no deflection. For complete demagnetization the current should not be reversed faster than once in $2t$ seconds.

This interval is not constant even for the same ring, but is longer in the region of greater permeability. In this region, therefore, the current should be reversed more slowly than at higher magnetizations. In every case the reversals should be slow enough to allow the flux to reach its full value before the next reversal. This rule allows faster reversals at the higher magnetizations.

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May 11, 1917.

THE WAVE-LENGTH OF LIGHT FROM THE SPARK WHICH EXCITES FLUORESCENCE IN NITROGEN.

BY CHARLES F. MEYER.

IT was shown by Professor Wood¹ in 1910, that radiations from the aluminium or copper spark are capable of exciting ultra-violet fluorescence in air and other gases, notably in nitrogen. The spark was passed between a rod serving as lower terminal, and a plate with a small hole in it serving as upper terminal, the spark striking just at the edge of the hole (Fig. 1). All the radiations from the spark, including the visible and ordinary ultra-violet, pass up through the hole in the plate, and if any of the radiations cause fluorescence this can be photographed by placing a camera off to one side of the opening. The luminosity was first photographed with a camera fitted with a quartz lens, and then with a quartz spectrograph which had had its slit removed, the fluorescent jet itself serving as slit.

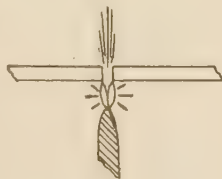


Fig. 1.

It was shown that the fluorescence in air consisted of the water bands 3064 and 2811, principally the former. When an atmosphere of nitrogen was used above the plate the water band 3064 appeared, and also the three nitrogen bands 3369, 3556 and 3778.

Inquiring now into the origin of the luminosity which exists above the opening, it is evident that the luminosity cannot arise from the simple scattering of light from the spark by particles of dust, or by the air molecules, as the spectrum of the luminosity is quite distinct from that of the spark, and a quartz plate several millimeters thick, placed over the hole, causes the light to disappear entirely.

That the fluorescence is excited by light in the Schumann or ultra-Schumann region was the first hypothesis proposed by Professor Wood, and in some work by Wood & Hemsalech² it was shown that the radiations were transmitted, but only to a slight degree, by a thin piece of clear fluorite. This fact indicated that the radiations exciting the fluorescence lay beyond the Schumann region, for the limit of the

¹ Phil. Mag. (6), Vol. 20, p. 707.

² Phil. Mag. (6), Vol. 27, p. 899, 1914.

Schumann region is set by the transmission of fluorite in sufficient thicknesses to form prisms and lenses.

Wood & Hemsalech also showed that the radiations exciting the nitrogen bands were transmitted to a slight degree through quartz, and in some experiments which Professor Wood and I performed,¹ we refracted the radiations through the extreme edge of an especially ground quartz prism, the path in the prism being probably less than a tenth of a millimeter. The index of refraction for the radiations came out $1.75 \pm .08$, that is, with a probable value greater than that of quartz at the more refrangible end of the ordinary ultra-violet. This value of the index of refraction made it seem as though the radiations were still on the long wave-length side of the quartz absorption band, and possibly not far beyond the limit of the Schumann region, if indeed they were beyond it at all. Unless it should be that they were on the long wave-length side of an entirely hypothetical second absorption band of quartz well beyond the Schumann region.

At this time we also succeeded in reflecting the radiations from silicon and speculum. The reflection experiment put me in mind of a method by which the wave-length of all or a part of the radiations might be approximately determined, in case they had a wave-length of seven or eight hundred angstroms or more.

The method is as follows: A very fine slot (.2 x 2 x 4 mm) is cut in a copper rivet, copper now being used for the spark terminals throughout. Beneath this is fastened a small fragment of a grating with the lines horizontal and parallel to the edges of the slot. The rivet serves as one spark terminal, a copper rod or wire as the other. Fig. 2 represents this arrangement in vertical section, *R* is the rivet with the slot in it. The rivet is driven through the thin copper plate *C*. *S* is the rod serving as the other spark terminal. *G* is the small fragment of a grating, the lines being perpendicular to the plane of the drawing. The plate *C* is bent into a right angle and fastened to an arm *A* which rotates on a horizontal axis. This rotation allows the plate, the rivet, and the grating, which are all fastened rigidly together, to be raised for the purpose of cleaning the grating. Below the grating and the lower end of the plate *C* is a thin horizontal plate with a rectangular hole in it 3 mm. by 4 mm. This second plate forms the top of a metal box into which nitrogen is introduced. The box also serves to keep out stray light and thus yield a dark background. The apparatus is represented in perspective in Fig. 3. The lettering of the parts is the same as in Fig. 2, only in addition attention is now called to the representation of the upper portion of the

¹ Phil. Mag. (6), Vol. 30, 1915.

box *B*, with the quartz window *W*, and some ten centimeters in front of the window the lens *L* and the prism *Pr*, and finally, off at a small angle, the photographic plate *P*. The path of the central ray through the optical system is indicated in the diagram. To avoid confusion in the diagram, a metal tube of about 2 cm. diameter, through which nitrogen

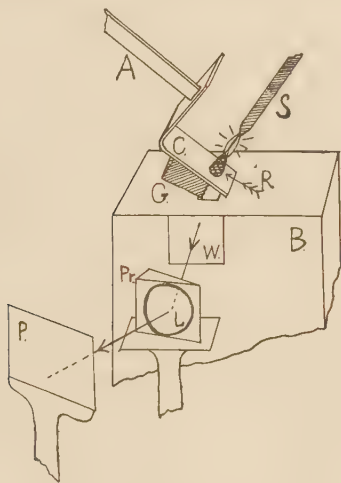


Fig. 2.

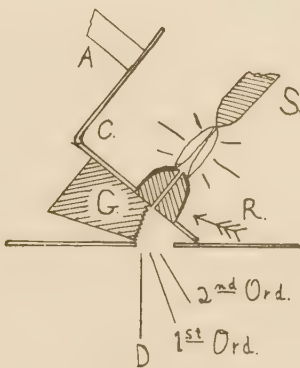


Fig. 3.

is introduced into the rear of the box *B*, has been omitted from the drawing. This tube also helps give an absolutely dark background, which is essential. None of the drawings are to scale, some dimensions being exaggerated for the sake of clearness.

Referring again to Fig. 2, it is seen that the beam of light, which comes through the slot in the rivet, strikes the grating at a large angle of incidence (73 deg.). The directly reflected beam comes off in the direction *D* in the figure. The first and second order diffracted beams come off in the directions indicated. The exciting light causes fluorescence along these three paths, and this fluorescence is photographed by the optical system represented in Fig. 3. The object of the 30 deg. prism *Pr*, is only to disperse the fluorescent light slightly and thus have a check on the nature of the spectrum, and to be certain that there is no scattered light. The prism is set for minimum deviation.

The dispersion caused by the prism would create confusion in the directly reflected and the diffracted beams if the fluorescent spectrum were a complicated one. But by using commercial nitrogen slightly moistened it is possible to limit the fluorescence to the water band 3064 alone. Moist nitrogen was used in the experiments.

The first experiment of this kind was made over a year ago, with a

grating of 15,000 lines to the inch. But the diffracting angle was not very great with this and it was felt that the experiment should be repeated. This has recently been done, using a grating of 30,000 lines to the inch. The results are much better, both on account of the more suitable grating and on account of improved technique. Measurements made upon two plates yield a result of 1300 Å., with a probable error of some 50 or 70 Å. This is for the wave-length of the light exciting the fluorescence of the water band 3064. The measures of course do not admit of much accuracy, as the beams of fluorescent light are not sharply bounded and not as intense as might be desired. The measures are made on the first order beam. An exposure of six or seven hours is necessary, the exposure being interrupted every half hour for cleaning the grating. The best plate shows also the second order diffracted beam quite unmistakably.

The experiment with the fluorescence in nitrogen was checked by placing a piece of cardboard in the chamber below the grating, the cardboard lying in the plane of the drawing (Fig. 2). The light scattered by the cardboard was photographed through the same optical system, but passing in addition through a film of silver on quartz which allowed only light of the wave-length of the silver transmission band to pass. The wave-length calculated in this manner for the transmission band of silver came out quite within the limit of experimental error.

As a result of the entire set of experiments it seems fairly certain that at any rate some of the radiations previously studied lie at the border of the Schumann region, and not beyond it. But it is difficult to account for the rather low transparency of good fluorite for the radiations, and the transparency of the air seems greater than would be expected. No actual measurements have been made of the transparency of the air. Professor Wood suggests that the fluorescence may be excited simultaneously by the radiations whose wave-length I have measured and by some of shorter wave-length which are not readily transmitted by fluorite or reflected by speculum metal. This may well be true.

It seems worth while, also, to consider the supposition that the radiations whose wave-length was measured are the only ones causing fluorescence. In this case it is necessary to suppose that the transparency of the fluorite is lessened, due to its proximity to the spark and consequent heating, and there remains to investigate the transparency of the air. It was hoped to do this, and to see whether there might possibly be an effect of the spark upon the transparency of the air in its immediate vicinity, but it has become necessary to lay the work aside for an indefinite period.

A rough estimate may be made from the reflection experiments of the coefficient of reflection of speculum metal for the region near $1300 \text{ \AA}$. It seems to lie between 5 and 10 per cent. at 75 deg. incidence.

In conclusion, I wish to thank Professor Wood for making several helpful suggestions.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
June, 1917.

THE MAGNETIZATION OF IRON IN THE ABSENCE OF HYSTERESIS.

BY WINTHROP R. WRIGHT.

ANY investigation of the magnetic properties of ferro-magnetic substances is complicated by the presence of hysteresis. Even the curve, usually known as the magnetization curve, is, as Steinmetz¹ points out, but one side of an unsymmetrical hysteresis loop, and differs from any other loop only in passing through the origin. The advantages to be gained in suppressing hysteresis are evident. Without hysteresis, the magnetization becomes a single-valued function of the magnetizing field and it is feasible to attempt an equation connecting them. Again, the true effect of the temperature upon magnetization may be investigated, for the effect of temperature upon hysteresis is so marked that its true effect upon magnetization may be entirely masked, especially in the case of weak fields.

In general, two methods have been proposed for suppressing hysteresis, mechanical shocks or vibrations and an alternating magnetic field, either transverse or longitudinal. Ewing² employed mechanical vibrations while Finzi,³ Ashworth,⁴ and Steinhaus and Gumlich⁵ used alternating fields superposed upon the magnetizing field. Ashworth alone investigated the change of magnetization with the temperature, but his results, while free from hysteresis, were distorted by the alternating field which was present in the specimen. Steinhaus and Gumlich avoided this distortion by reducing the alternating field to zero before observing the magnetization produced in the specimen due to the applied magnetizing field.

¹ Steinmetz, *Theory and Calculation of Electric Circuits*, p. 50.

² Ewing, *Phil. Trans.*, p. 564, 1885.

³ Finzi, *Electrician*, 26, 672, 1891.

⁴ Ashworth, *Phil. Mag.*, 27, 357, 1914.

⁵ Steinhaus and Gumlich, *Ber. d. Deut. Phys. Ges.*, 17, 369, 1915.

The present work is, in a sense, a repetition of Ashworth's work on iron, using the method of Steinhaus and Gumlich. Five specimens were prepared from samples furnished through the kindness of Professor E. D. Campbell. These included three hypo-eutectoid steels, a very pure basic open-hearth steel, and an ingot iron. Their composition was furnished with them and appears in Table I. These five form a series of steels with decreasing carbon content whose last member approximates pure iron. The specimens were made in the form of ellipsoids of revolution, 20 cm. long and 0.47 cm. in diameter.

TABLE I.
Composition of Steels in Per Cent.

Steel.	C.	Mn.	P.	Si.	Cu.	S.
H57.....	0.57	0.11	0.010	0.17		0.020
H41.....	0.41	0.08	0.012	0.19		0.016
H35.....	0.35	0.08	0.009	0.18		0.024
04.....	0.04	0.10	0.007			0.029
INI.....	0.015	0.016	0.005		0.045	0.03

APPARATUS.

A magnetometer was used for observing the magnetization of the specimen. Two identically wound solenoids were mounted east and west with the principal needle of the magnetometer on their common axis and between them. These solenoids were made of brass tubes, 4 cm. in diameter, with a layer, 60 cm. long, of No. 20 enamelled copper wire wound on them. They made available magnetizing fields up to 100 gauss in strength. The one solenoid, which was used for magnetizing the specimen, had a second layer wound on it, by which the required alternating field could be produced. Each solenoid was mounted in a copper tank which was water cooled. The second solenoid was used to balance the first and could be shifted longitudinally.

The magnetometer was of the astatic type devised by Kohlrausch and Holborn.¹ The moving system consisted of two sets of two needles each, 2.0 cm. long and 0.09 cm. in diameter, mounted at the ends of a glass rod, 70 cm. long and 0.1 cm. in diameter, and was suspended by a quartz fiber, 40 cm. long and 30 microns in diameter. Though the upper needles were slightly stronger, the instrument possessed a steady zero point and was sufficiently sensitive, a field of 0.00005 gauss causing a scale deflection of 2 mm. with a scale distance of 1.5 m. As the magnetometer was to be used in a null method, these were the only require-

¹ Kohlrausch and Holborn, *Ann. d. Phys.*, 10, 287, 1903.

ments to be met and it was not necessary to ascertain to what extent the needle systems differed.

The magnetization produced in the specimen was measured by means of a coil, mounted on the side of the magnetometer opposite to the specimen and at an equal distance. By passing a suitable current through this coil, the deflection produced by the magnetization of the specimen was balanced and the needles of the magnetometer were brought back to their zero position, which was indicated by the familiar lamp, slit, mirror, and scale device. The magnetization of the specimen could then be calculated in terms of the current and the constants of the coil and the ellipsoid. The coil was made by winding No. 20 enamelled copper wire upon a core of Keene cement, a disc 17.3 cm. in diameter and 3.1 cm. thick. A slot was cut on the rim of the disc and a single layer of wire wound on it. This layer was covered with more cement and a new surface was cut after the cement had hardened. On this new surface, a second layer was wound and the process was repeated until five layers had been put on, separated from each other by from two to four millimeters of cement. This method of assembling the coil permitted the accurate measurement of the dimensions of each layer and the field of the coil could be calculated from the formula for a single layer.

The data taken for a given magnetization curve involved the determination of the corresponding values of two currents, that through the magnetizing solenoid and that through the coil. This method for determining the magnetization seems to have much in its favor. It is independent of changes in the sensitivity of the indicating instrument and in the strength of the earth's field, even if the magnet systems are not exactly equal and are not accurately placed in the magnetic meridian. It replaces readings of a telescope and scale with those of a second ammeter, one having to be read for the magnetizing current, and thus affords two observations of the same type. It would seem that there is no difference in the rapidity with which observations can be taken since this depends so largely on the period and damping of the magnetometer in any method.

A 60-cycle alternating current, regulated by means of a water rheostat, was used in the outer winding of the magnetizing solenoid to produce the requisite alternating field. This rheostat had two electrodes of copper whose area was about 150 cm.² and, by lifting the movable electrode, the current could be reduced from about ten amperes to a few hundredths of an ampere before the final break occurred. It may be questioned whether such a device for reducing the current is legitimate, since it does involve a break in the current, though not until the latter

is small. By this means, however, the same magnetization was produced in the specimen for a given field, though the initial state was varied as widely as possible, and this should be a conclusive test for the absence of hysteresis. An objection to the rheostat may also be based upon its rectifying action due to inequality in the areas of the electrodes as the movable one is removed from the water. It was found, however, that the magnetization did not depend upon the direction of the rectified current through the solenoid. Evidently, when the alternating current became small enough to be neglected, the rectified portion was also negligible.

The specimen was heated by means of an electrical heater which fitted snugly within the brass tube of the magnetizing solenoid. The heating wires were of 25 per cent. nickel-steel and ran longitudinally, being held in place by alundum cement at equal spaces around the heating chamber. The latter was 60 cm. long and 1 cm. in diameter. A longitudinal winding produced no magnetic field within the heating space and secured a more uniform temperature throughout that part in which the specimen lay. The necessary thermal insulation was secured by two concentric quartz tubes, separated by asbestos, which slipped over the hollow alundum cylinder in which the wires were set. The heater was slightly magnetic below 500° C. but separate observations were taken to correct for this.

The ends of the magnetizing solenoid were provided with brass cover plates, made oil tight with asbestos gaskets. Through one plate passed a brass plug in which were mounted the tubes for a platinum resistance thermometer. The thermometer wire with its leads was stretched in a quartz tube, 1 mm. in bore, which was then bent double. The wire was long enough to traverse the length of the specimen twice, the latter being supported by the same tube which contained the wire. The compensating leads were mounted in a shorter piece of the same tubing. With such a thermometer the average temperature throughout the specimen was indicated.

EXPERIMENTAL RESULTS.

The usual procedure with a specimen began with heating it for about an hour and a half in the neighborhood of the Curie point in order to anneal the specimen and to secure thermal equilibrium in the heater, solenoid, and oil bath. The temperature was then reduced slowly, step by step, and magnetization curves were taken at suitable intervals. The greatest change in magnetization occurred within the first one hundred degrees below the Curie point and from four to five hours were

allowed for this interval. About twice this time was taken for the specimen to cool completely to room temperature. Measurements were taken during cooling that they might be more free from irregularities due to previous thermal and mechanical treatment of the steels.

The magnetization curves obtained for specimen H35, the softest of the hypo-eutectoid steels, appear in Fig. 1. These are typical of the

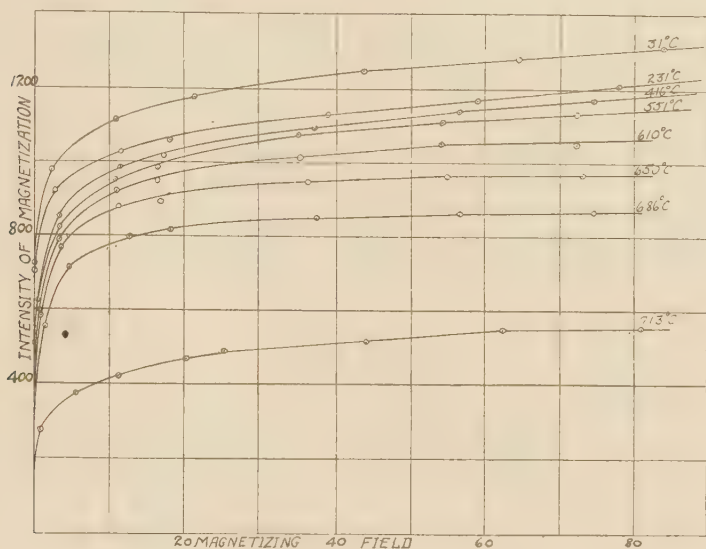


Fig. 1.

isothermals obtained for all five steels. The abnormally high susceptibility for low magnetizing fields, which seems to be the most pronounced characteristic of anhysteretic curves, persists up to the immediate neighborhood of the transformation point. The curves are uniformly concave to the H -axis and do not intersect each other except at the origin, though the curves are not conclusive on this latter point. The true magnetizing field is obtained as the difference between the applied field and the demagnetizing field due to the ellipsoid itself and this results in relatively great uncertainty in the value of H when the field is weak. In the case of the softest of the steels, this difference was less than the error in the observations for applied fields as large as ten gauss and intensities of magnetization as high as nine hundred.

If, as seems likely, any given isothermal lies wholly beneath any other which corresponds to a lower temperature than the former, the magnetization for a given field decreases with a rise in the temperature. In the absence of hysteresis we do not find the anomaly common to ordinary magnetization curves, namely, that the magnetization for a given field

may either increase or decrease with rise of temperature, depending upon whether the field is weak or strong. In Fig. 2 are found the magnetization curves for all five specimens for a constant field of sixty gauss. It is evident that the curve for specimen *INI*, which is most nearly free from carbon, is by far the most regular. The effect of carbon is to produce two irregularities, the one just above 700°C . and the other in the neighborhood of 200°C . The former corresponds to the precipitation of the carbides which occurs at the eutectoid point. The latter is due to the magnetic transformation of the cementite in the steel. The actual shape of the curves at this lower transformation point is not definitely indicated by the data but must be somewhat as shown by the dotted portions. The transformation point certainly lies between 180°C . and 220°C . which agrees with Honda's¹ work on cementite. For the purpose of the present investigation, a more exact knowledge of the curves in this region was not necessary.

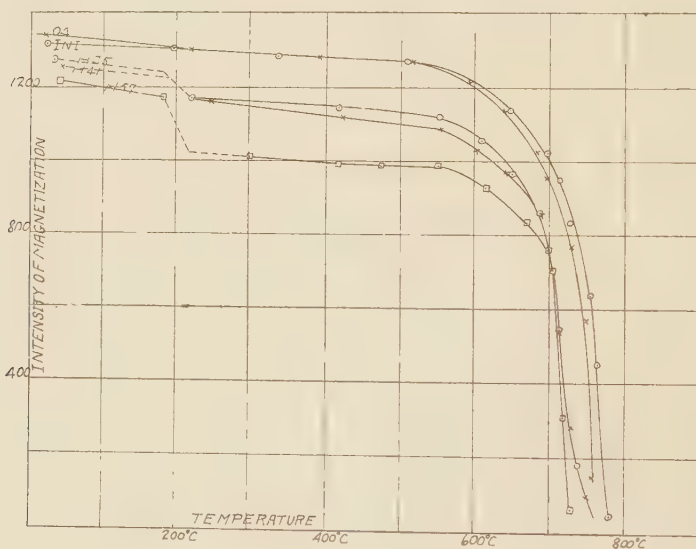


Fig. 2.

EQUATIONS FOR ANHYSTERETIC CURVES.

Examination of the curves in Fig. 1 shows them to be smooth and regular, whether they are for iron or steel. The curves have at least three distinguishing characteristics, a uniform concavity to the H -axis, an infinite slope at the origin, and a finite limit to the ordinate as the abscissa increases indefinitely. The curves, of course, furnish no con-

¹ Honda and Takagi, Journ. Iron and Steel Inst., 92, 181, 1915.

clusive proof of the third characteristic but they indicate nothing contrary to this, the ordinarily accepted view. The appearance of the isothermals suggests the possibility of obtaining an equation for a given curve. But Fig. 2 shows clearly that to introduce the temperature as a variable in the equations will be feasible only in the case of carbon-free iron.

The only equation yet proposed for anhysteretic isothermals is empirical and due to Fröhlich. Finzi and Ashworth (*loc. cit.*) have both attempted to apply this equation to their experimental results. Steinmetz¹ has shown that the same equation may be fitted to limited ranges of the ordinary magnetization curve and expresses his opinion that it should probably fit an anhysteretic curve throughout its whole extent. The equation is based upon the assumption that the susceptibility is proportional to the amount by which the magnetization may yet be increased. Expressed in symbols, this becomes

$$\frac{I}{H} = K(I_0 - I),$$

where I_0 is the maximum intensity of magnetization and K a constant. This may be transformed into the more useful form

$$H \left(\frac{1}{I} - \frac{1}{I_0} \right) = A,$$

where A is a new constant. This equation is hyperbolic in H and I , but is linear in H and H/I . In Fig. 3, the data of Fig. 1 are plotted with this second pair of variables as coördinates and it may be seen to what extent the linear relation holds. Where a straight line fails to fit the points, a continuation, either straight or curved, has been made which will do so, in order that there may be less confusion as to corresponding lines and points. The continuations have been indicated by the dotted lines. In none of the isothermals does the equation seem to hold for fields much less than twenty gauss and, in two, at least, there is an indication that the relation is not linear through the upper range of available fields. This failure of the equation to hold may be considered from another viewpoint. If we form the derivative from the equation, we obtain

$$\frac{dI}{dH} = \frac{1}{A} \left(1 - \frac{I}{I_0} \right)^2.$$

¹ Steinmetz, *Theory and Calculation of Electric Circuits*, p. 54.

At the origin, this becomes

$$\left(\frac{dI}{dH}\right)_0 = \frac{I}{A}$$

and the condition for infinite slope can be fulfilled only by making A vanish, which would reduce the hyperbola to two straight lines.

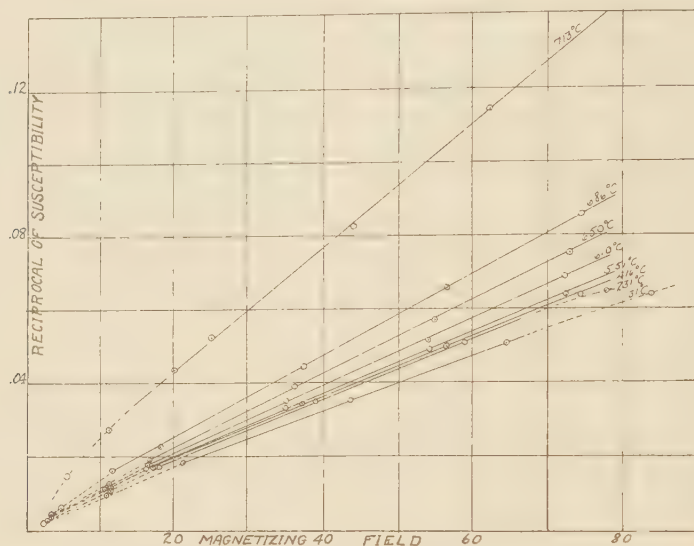


Fig. 3.

The results indicate that Fröhlich's equation does not fit the an-hysteretic isothermal magnetization curves, though it may be made to fit a limited range of any curve and may be used as an approximation for the curve. Ashworth¹ not only accepts Fröhlich's equation for a given isothermal but attempts to use it for the whole family by introducing the temperature as a third variable. He does this from analogy with Van der Waal's equation and writes Fröhlich's equation in the form

$$H \left(\frac{I}{I} - \frac{I}{I_0} \right) = RT,$$

where R is a constant and T the absolute temperature. For H constant, this equation is hyperbolic in T and I . But the hyperbola of the equation is convex toward the T -axis whereas the curves of Fig. 3 are concave. This difficulty might be met by assuming that I_0 is a function of the temperature but, since it is an unknown function, it does not seem that Ashworth's equation is a step in advance of that of Fröhlich.

¹ Ashworth, loc. cit.; also Phil. Mag., 33, 349, 1917.

SUMMARY.

1. A null method for using the magnetometer has been described.
2. From a series of steels with decreasing carbon content, the anhysteretic magnetization curves for iron have been approximated and certain characteristics of these curves have been pointed out.
3. It has been shown that the equation proposed by Fröhlich does not fit the anhysteretic isothermal magnetization curves and that the equation, even when modified as Ashworth proposes, does not give the magnetization properly related to the temperature.

In conclusion, the writer wishes to acknowledge his indebtedness to the late Professor K. E. Guthe, at whose suggestion the work was undertaken, and to the members of the department of physics of the University of Michigan.

UNIVERSITY OF MICHIGAN,
May, 1917.

THE ABSORPTION OF NEAR INFRA-RED RADIATION BY WATER-VAPOR

BY W. W. SLEATOR

I. INTRODUCTION

The study of the absorption of radiation in the atmosphere was begun by Langley,¹ whose holographs, or maps of the sun's spectrum, show wide bands attributed by him to water-vapor. Paschen,² in work on the emission of radiation by gases, has investigated as well the absorption occurring in steam, and records in particular the effect of changes in temperature upon the wave-lengths of the radiation absorbed. His work has been extended by Eva von Bahr,³ who has shown that the doublet between wave-lengths 5 and 7 μ is in reality very complex and contains about forty separate absorption bands arranged with some appearance of symmetry on either side of the wave-length 6.26 μ .

The combination principle suggested by Bjerrum,⁴ in connection with his application to the case of molecular rotation of the quantum theory, is a fruitful hypothesis in the explanation of near infra-red absorption. Bjerrum's ideas have in fact been applied by Eucken⁵ to the system of water bands presented in the work of Eva von Bahr, and that system seems to be accounted for in terms of two series of rotation-frequencies corresponding to two principal moments of inertia in the water molecule. More recent work by Rubens and Hettner⁶ shows some evidence for the presence in the farther infra-red of a third series of rotation-frequencies. The

¹ *Researches on Solar Heat* (Professional Papers of the Signal Service, No. 15, United States War Department).

² *Annalen der Physik*, **51**, 4, 1894; **52**, 210, 1894; **53**, 234, 1894.

³ *Phil. Mag.*, **28**, 71, 1914; *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 731, 1913.

⁴ *Nernst Festschrift*, p. 90.

⁵ *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 1159, 1913; *Phil. Mag.*, **28**, 71, 1914.

⁶ *Chemical Abstracts*, **11**, 1357, 1917; *Science Abstracts*, No. 234, p. 223, June 1917.

question of molecular structure is now intimately connected with the investigation of radiation, as is shown by further work of Bjerrum,¹ and important tests of the quantum hypothesis await experimental advances in the same field.²

The present paper gives an account of work undertaken to extend our knowledge of atmospheric absorption. It concerns particularly the region of the spectrum between the wave-lengths 1.3 and 3μ and presents a detailed study of the absorption regions marked Ψ , Ω , and X on Langley's charts.

II. APPARATUS

The work of Eva von Bahr was done with a prism spectrometer and radiomicrometer. In the work recounted here a higher dispersion was secured by the use of gratings, and the uncertainty of wave-lengths determined with the aid of a dispersion-curve was at the same time avoided. The troublesome overlapping of grating spectra has been eliminated by the use of a supplementary prism. The general arrangement is shown in Fig. 1. The apparatus takes the form of two spectrometers, each with fixed arm and single mirror.³ By a proper setting of the prism a definite and limited portion of the spectrum is presented to the grating spectrometer. The prism serves in fact as an effective screen or filter.

A linear thermopile, incased at T in Fig. 1, and a galvanometer of the Paschen type constituted the detecting system. The ballistic deflections of the galvanometer observed on opening or closing the shutter at O serve to map out the spectrum of the Nernst glower used as the source of energy. The construction of the galvanometer was the first work done on the present problem.

The entire path of the light, shown in Fig. 1 by the dotted lines, is inclosed in a black box of double cardboard. It is of course not possible to make such a box tight, nor to get the air in it absolutely dry. In the section around the glower, however, the air could be saturated. Also energy-curves were plotted from data secured on winter nights, when cold air from out of doors was pumped through

¹ *Verhandlungen der deutschen Physikalischen Gesellschaft*, **16**, 737, 1914.

² *Ibid.*, **16**, 614, 1914; **15**, 1159, 1913.

³ *Annalen der Physik*, **33**, 739, 1910.

sulphuric acid and phosphorus pentoxide into the cases. Sufficient difference appeared between the depths of the bands to enable us to attribute the absorption to water-vapor.

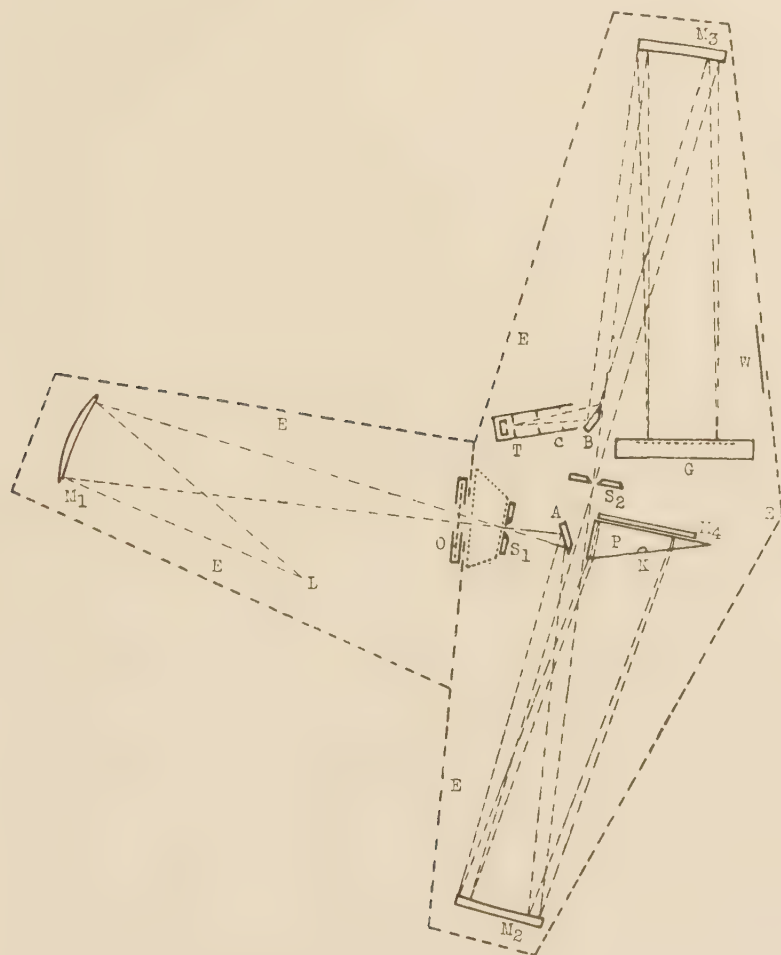


FIG. 1.—The spectrometer, scale 1 to 5

L, Nernst glower; *S*₁, *S*₂, slits; *M*₁, 10 cm mirror, *f*=20 cm; *P*, salt prism; *M*₂, *M*₃, 10 cm mirrors, *f*=50 cm; *M*₄, *A*, *B*, plane mirrors; *G*, grating; *C*, case for *T*, the thermopile; *W*, window in box *E*; *O*, shutter. The path of the light is *LM*₁*S*₁*AM*₂*PM*₄*PM*₃*S*₂*M*₃*GM*₃*BT*. A spectrum appears at *S*₂. *P* and *M*₄ rotate together about *K*, so that any region of the spectrum may be isolated for the grating, and the overlapping of spectra is avoided.

In the region of the spectrum near the wave-length 2.6μ some work has been done with steam. The absorption took place in a chamber 15 cm long, which was kept hot by resistance coils, and could be swung into or out of the beam of light. The glass ends of the chamber were compensated for by two pieces cut from the same

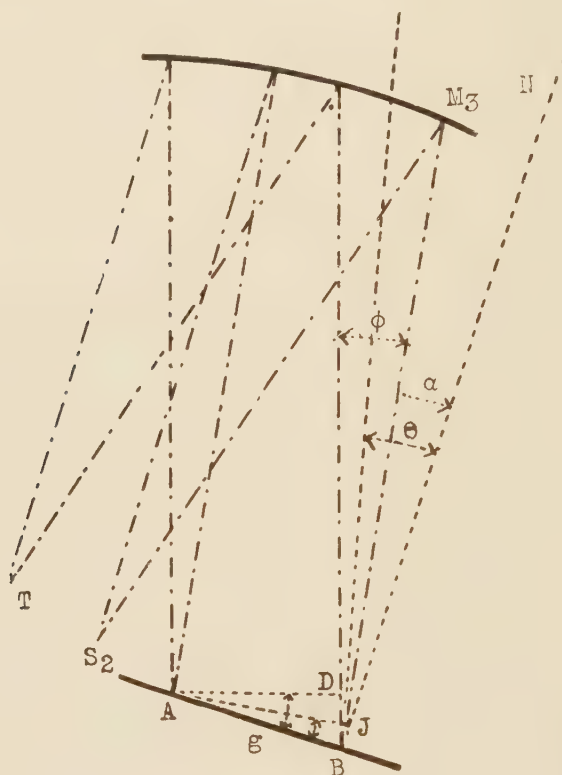


FIG. 2.—The spectrometer constant κ in the equation $\lambda = \kappa \sin \theta$

AB is the grating space, g . Light from S_2 is sent to T . T , S_2 , and M_3 , the mirror, are fixed, and rotation of the grating leaves ϕ unchanged. The wave-length at T is determined by the relation $n\lambda = DB + BJ$

$$\begin{aligned} &= g \sin (\alpha + \phi) + g \sin \alpha \\ &= 2g \sin (\alpha + \tfrac{1}{2}\phi) \cos \tfrac{1}{2}\phi \\ &= 2g \cos \tfrac{1}{2}\phi \sin \theta \\ &= \kappa \sin \theta \end{aligned}$$

$\theta = \tfrac{1}{2} (R_1 - R_2)$, R_1 and R_2 being circle readings on the two spectra of one order.

sheet of glass, through which the radiation passed when the steam chamber was drawn aside.

Three gratings have been employed in the course of the work. The smallest has a ruled surface 5 cm wide and about 2400 lines to the inch, and is referred to as the brass grating. The other two have effective surfaces 12.2 cm wide, are ruled on speculum metal, and are referred to as the 7500-line grating and the 15,000-line

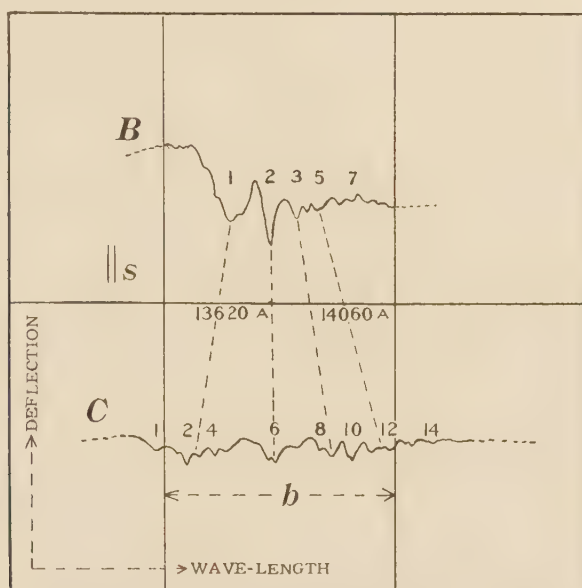


FIG. 3.—Energy-curves, region of 1.3μ . The slit corresponds to 33 Å in B and 15 Å in C.

grating, the figures giving the number of lines per inch. In Figs. 3, 4, 5, and 6 the letters A, B, and C refer respectively to these gratings. They are mounted on the table of a Schmidt and Haensch spectrometer whose circle may be read to ten seconds.

Fig. 2 serves to illustrate the meaning and derivation of the equation

$$\lambda = \kappa \sin \theta,$$

used in computing wave-lengths from data secured with the fixed-arm spectrometer. To obtain the wave-length interval included at

one time in the slit of the thermopile, one considers first the resolving power of the grating. If the source S_2 were very narrow, the width of the central bright band in the diffraction pattern produced by monochromatic light would be given by

$$w = \frac{2\lambda}{b \cos \theta} \cdot 500,$$

where b is the width of the grating in mm, θ the angle by which the grating is turned from the normal, and 500 the focal length of the

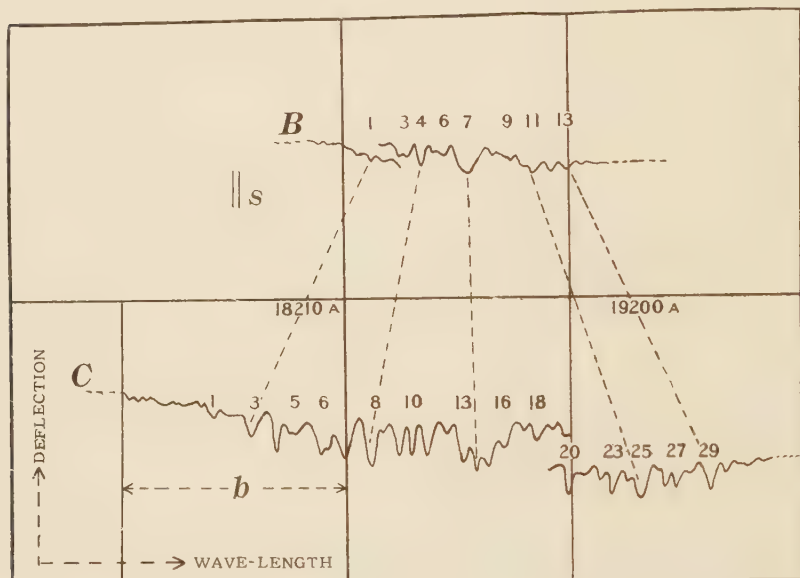


FIG. 4.—Energy-curves, region of 1.8μ . The slit corresponds to $33 \text{ \AA}$ in B and $14 \text{ \AA}$ in C .

mirror in mm. For the 15,000-line grating w is 0.03 mm at 2.6μ , and for the brass grating 0.14 mm at 6μ . The slit S_2 is $\frac{1}{2} \text{ mm}$ wide, and its image in the plane of the slit of the thermopile is in the first case about 0.52 mm and in the second about 0.57 mm wide. With the slits now in use no great improvement in the purity of the spectrum can be attained by enlarging the grating.

The range of spectrum included in the slit is taken as the interval in wave-lengths between two beams whose centers are $\frac{1}{2} \text{ mm}$ apart

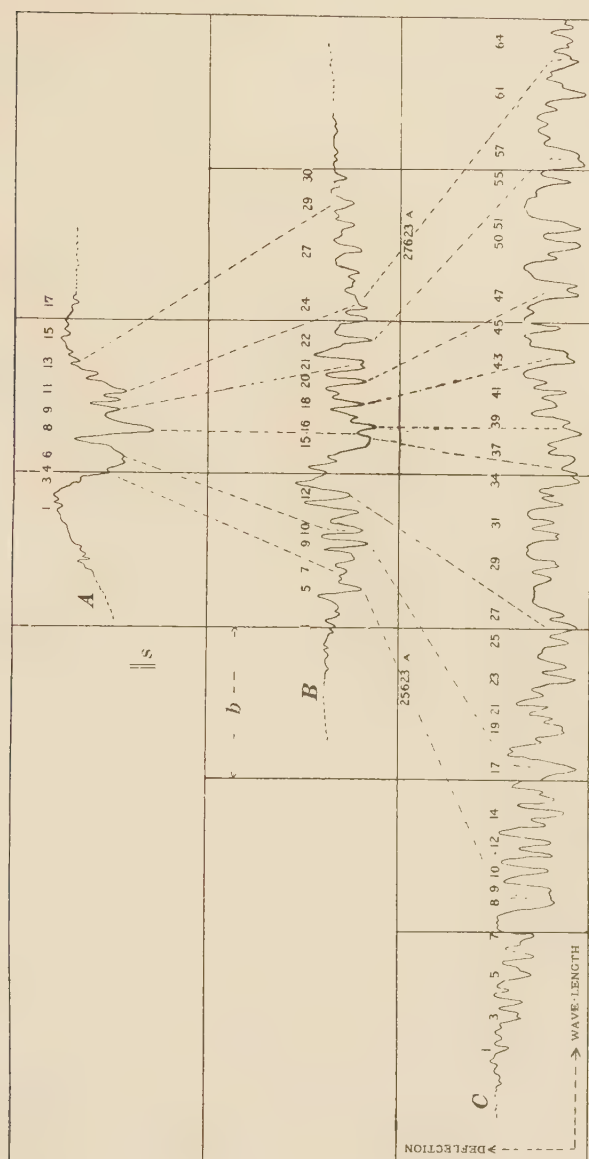


FIG. 5.—Energy-curves, region of 2.6μ . The slit corresponds to $105 \text{ \AA}$ in A, to $31 \text{ \AA}$ in B, and to $11 \text{ \AA}$ in C. C does not give the entire curve of this region, as explored with the 15,000-line grating.

in the plane of the thermopile. That slit does not take in the total energy even of a single wave-length, but does receive about three-fourths of the energy in the interval named. This interval corre-

sponds to a variation in ϕ (in Fig. 2) of $\frac{1/2}{500}$ or 0.001 radian.

Taking the equation for wave-length as

$$\lambda = 2g \cos \phi/2 \sin (\alpha + \phi/2),$$

and considering that $\phi/2$ is found by measurement to be $1^\circ 16'$, we have by differentiation the approximation

$$\begin{aligned} d\lambda &= K \cos \theta d\theta \\ &= K \cos \theta \frac{d\phi}{2}. \end{aligned}$$

This expression gives the values set down with the figures, which are a little too large. In order to throw a single beam from one



FIG. 6.—Energy-curve, part of the region of 6 μ . The slit corresponds to 100 Å

side of the slit of the thermopile to the other, ϕ must be changed by $\frac{1/2}{500}$ or 0.001 radian, as above, and this demands a change

in α of 0.0005 radian and a corresponding motion of the grating. 0.0005 radian is $1'7$, and the spectrum interval may be checked by noting the value of $1'7$ in units of wave-length along an energy-curve. At 2.6 μ the 15,000-line grating gives this interval as 10.4 Å.

The green line of the spectrum of mercury ($\lambda = 5460.74$ Å, Kaye and Laby's tables) was used for visual calibration, the bright line and the slit of the thermopile being viewed objectively. In the case of the brass grating no visible lines could be observed, but the actual grating-space was known, and

$$K = 2g \cos \frac{1}{2}\phi$$

was computed from data obtained from measurement.

III. THE CURVES

Figs. 3, 4, 5, and 6 present a summary of the experimental work. Except in Fig. 6 each energy-curve is one of three secured, for two of them the air being saturated and for one dried. The bands are numbered arbitrarily for reference to the tables. The letters *A*, *B*, and *C* refer respectively to the brass, the 7500-line, and the 15,000-line grating. In Fig. 7, as well as in the others, the distance *b* denotes 1° on the circle and *s* shows the relative size of the thermopile slit.

Fig. 7 represents part of the region at $2.6\ \mu$ as mapped with the 7500-line grating. The upper curve (lettered *D*) does not show the galvanometer deflections but gives the percentage of incident energy transmitted by steam. The effect of drying the air appears also in this figure, in curve *E*, and it will be noted that the curve for steam accentuates the peculiarities of *F*, the "air-saturated" curve, peculiarities which the curve secured with dried air decidedly obscures. It seems that the temperature of the absorbing vapor has no effect on the position of an individual band. According to Paschen's work, already cited, we conclude that the relative intensities of the bands must change, so that those that are deepest at one temperature are not deepest at another. But the present work cannot confirm nor deny this effect. The effect on the absorption of drying the air, shown in Fig. 7, was found even more definitely with the finer grating, at 1.3 and $1.8\ \mu$, as well as at $2.6\ \mu$. All the deeper bands are less marked when the air is dry. This does not appear so clearly with the shallow bands, but it may be that in the "air-saturated" curves the presence of weak bands is masked by their more prominent neighbors. It is upon such evidence as appears in Fig. 7 that we ascribe the absorption to water-vapor.

With the 7500-line grating the intervals of the spectrum between the absorption bands at 1.3 and $1.8\ \mu$, and between those at 1.8 and $2.6\ \mu$, were carefully explored and were found to present no evidence of atmospheric absorption.

In Figs. 3 and 5 the upper curves are decidedly similar. This similarity suggests that one of these absorption regions may be a harmonic of the other in the sense suggested by Kemble.¹ However,

¹ *Physical Review*, **8**, 689, 1916.

a frequency half that corresponding to band No. 2 in Fig. 3 corresponds nearly to band No. 11 in Fig. 5 rather than to band

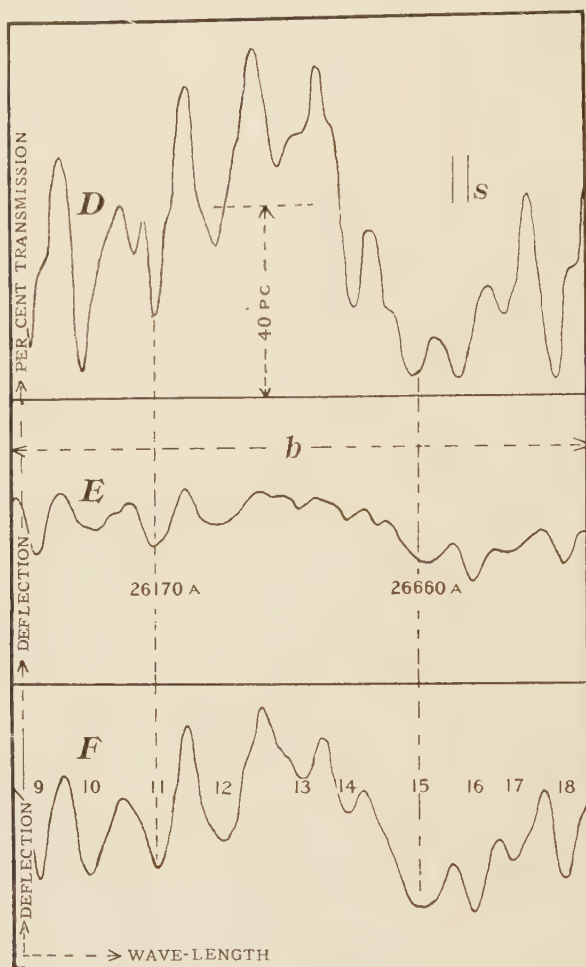


FIG. 7.—Part of the region of $2.6\ \mu$, 7500-line grating. *D* gives the percentage of energy transmitted by steam at 110 to 120° C. and 1 atmosphere pressure. *E* is an energy-curve with the air partly dried, *F* an energy-curve with the air saturated at about 35° C.

No. 8, and the same lack of agreement appears in the lower curves. Evidently the simple idea of harmonics does not apply.

A comparison of the energy-curves in Fig. 5, secured respectively with the 7500- and 15,000-line gratings, shows how the increased dispersion adds to our knowledge of the absorption. Bands No. 8 and No. 9 in the lower curve, for example, appear in the middle one as No. 5, a connection indicated in typical cases by the dotted lines, and appearing more definitely in the tables. These curves must be considered in any numerical computations made with absorption frequencies, for in the curves appear the individualities of the bands, which cannot well be expressed in numbers. In all cases the grating was turned $1'$ for each new setting. At 6 and at $2.6\ \mu$ six deflections were taken at each minute, and at 1.3 and $1.8\ \mu$ four. The computations are based on curves which, for the region at $2.6\ \mu$, are about six feet long.

IV. THE TABLES

On pages 137 to 142 are set forth the wave-lengths and frequencies of the bands, which are denoted by the numbers given with the curves. Corresponding wave-lengths appear opposite each other. The gratings have been calibrated independently, the values given have been calculated from independent curves, and the agreement between opposite numbers is in general satisfactory. In connection with the region of $6\ \mu$ is set forth some evidence of the symmetry demanded by Eucken's explanation, but unfortunately the work was not carried far enough to give this evidence much value. Some idea of the accuracy of the determinations of λ and N might be obtained by estimating the effects of various sources of error. But first one may consider the different values secured for the same quantity from the three corresponding curves. The "typical computations of λ and N " show these numbers for certain bands in the region at $2.6\ \mu$ —bands taken quite at random. Considering the uncertainty in the value of K we should perhaps affect the wave-length by the probable error of $\pm 2\ \text{\AA}$. Errors in the circle of the spectrometer are probably negligible, especially since the calibration involved the same sections of the circle as were employed in the measurements. At $6\ \mu$, where we have only one curve, obtained under less favorable circumstances, we should perhaps write the wave-lengths with an error $\pm 20\ \text{\AA}$. A question mark in the tables

TYPICAL DATA

The settings of the grating circle, and corresponding deflections of the galvanometer.

2 A.M., March 22, 1917. Grating temperature, 27°. Period of galvanometer, 6 secs.; E.M.F. applied to glower, 238 volts.

Circle	Deflections in mm	Circle	Deflections in mm
121° 10'.....	28-9- 9-8-9-9=28.7	120° 58'.....	18- 9- 8-9-9-9=18.7
9'.....	26-7- 7-6-7-6=26.5	57'.....	19-20- 0-0-0-0=19.8
8'.....	23-2- 1-2-2-2=22.0	56'.....	16- 7- 8-8-8-7=17.3
7'.....	12-5- 6-6-4-5=14.7	55'.....	9-11-10-1-0-1=10.3
6'.....	11-2- 3-2-3-1=12.0	54'.....	10- 0- 1-0-1-1=10.5
5'.....	10-2- 2-1-2-2=11.5	53'.....	18-22- 0-1-0-1=20.3
4'.....	15-8- 7-7-8-7=17.0	52'.....	24- 6- 5-5-6-5=25.2
3'.....	17-6- 6-7-6-7=16.5	51'.....	27- 7- 6-7-7-7=26.8
2'.....	9-8-10-9-9-8= 8.8	50'.....	27- 8- 6-7-6-8=27.0
1'.....	5-5- 4-5-5-6= 5.0	49'.....	25- 7- 6-8-6-7=26.5
121° 0'.....	6-6- 5-6-6-6= 5.8	48'.....	23- 6- 4-6-4-6=24.8
120° 59'.....	14-3- 4-3-4-3=13.5	47'.....	22- 3- 1-4-2-3=22.5

TYPICAL COMPUTATIONS OF WAVE-LENGTH AND FREQUENCY

REGION OF 2.6 μ

Band No.	Curve No.	λ	Mean λ	N	Mean N
20.....	{ 1	26063.4	26066.2	383.60	383.64
	{ 2	26068.8		383.60	
	{ 3	26066.5		383.63	
23.....	{ 1	26162.7	26161.6	382.22	382.24
	{ 2	26161.7		382.25	
	{ 3	26160.4		382.26	
27.....	{ 1	26321.3	26325.5	379.92	379.86
	{ 2	26330.0		379.79	
	{ 3	26325.3		379.86	
31.....	{ 1	26543.7	26546.4	376.74	376.70
	{ 1'	26546.9		376.70	
	{ 2	26549.3		376.66	
	{ 3	26545.7		376.71	
32.....	{ 1	26587.4	26589.8	376.12	376.08
	{ 1'	26589.5		376.09	
	{ 2	26590.9		376.07	
	{ 3	26591.4		376.06	
33.....	{ 1	26608.7	26609.9	375.82	375.80
	{ 1'	26610.9		375.79	
	{ 2	26610.2		375.80	
	{ 3	26609.7		375.80	

denotes not a doubtful band but a doubtful correspondence. The second column in the tables for the region at $2.6\ \mu$ gives the relative depths of the bands as an indication of their importance in other infra-red work. A band numbered 1 seems to represent an absorption of less than 10 per cent, while 5 shows that perhaps 80 per cent of the incident energy is absorbed.

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM

REGION OF $1.38\ \mu$

15,000-LINE GRATING			7500-LINE GRATING		
Band No.	Wave-Length μ	Wave No. per mm	Band No.	Wave-Length μ	Wave No. per mm
1	13545	738.3			
2	13614	734.5	1	13620	734
3	13643	733.0			
4	13678	731.1			
5	13710	729.4			
6	13820	723.6	2	13820	723.5
7	13876	720.7			
8	13922	718.3			
9	13954	716.7	3	13950	717
10	14000	714.3	4	14010	714
11	14046	712.0	5	14060	711
12	14092	709.7			
13	14140	707.2	6	14170	706
14	14186	704.9	7	14240	702

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

REGION OF $1.87\ \mu$

15,000-LINE GRATING			7500-LINE GRATING		
Band No.	Wave-Length μ	Wave No. per mm	Band No.	Wave-Length μ	Wave No. per mm
1.....	18110	552.2			
2.....	18152	550.9			
3.....	18202	549.4	1	18210	549.1
4.....	18263	547.6			
5.....	18306	546.3	2	18287	546.8
6.....	18363	544.6			
7.....	18414	543.1	3	18398	543.6
8.....	18471	541.4			
9.....	18534	539.6	4	18467	541.5
10.....	18564	538.7	5	18530	539.7
11.....	18595	537.8			
12.....	18641	536.4	6	18590	537.9
13.....	18676	535.5			
14.....	18705	534.6			
15.....	18729	533.9	7	18704	534.6
16.....	18765	532.9			
17.....	18806	531.8			
18.....	18836	530.9	8	18836	530.9
19.....	18862	530.2			
20.....	18897	529.2			
21.....	18926	528.4	9	18912	528.8
22.....	18968	527.2			
23.....	18995	526.5	10	18987	526.7
24.....	19022	525.7			
25.....	19054	524.8	11	19038	525.3
26.....	19106	523.4			
27.....	19133	522.7			
28.....	19157	522.0	12	19126	522.9
29.....	19199	520.9			
30.....	19234	519.9	13	19195	521.0
			14	19264	519.1

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

REGION OF $2.6\ \mu$

15,000-LINE GRATING				7500-LINE GRATING			HILGER BRASS GRATING		
Band No.	Relative Intensity	Wave-Length A	Wave No. per mm	Band No.	Wave-Length A	Wave No. per mm	Band No.	Wave-Length A	Wave No. per mm
1.....	I	25235	396.28				?1	24850	402.2
2.....	I	25262	395.85				?2	25040	399.4
3.....	2	25311	395.09						
4.....	2	25352	394.45	I	25347	394.52			
5.....	2	25425	393.31	2	25432	393.21			
6.....	2	25469	392.63	?3	25481	392.45	?3	25490	392.2
7.....	2	25520	391.85	4	25517	391.90			
8.....	3	25608	390.50						
9.....	3	25636	390.08	5	25623	390.27			
10.....	3	25688	389.29	6	25696	389.17			
11.....	3	25727	388.70						
12.....	3	25760	388.20	7	25747	388.39			
13.....	2	25803	387.55				4	25760	388.2
14.....	4	25830	387.15	8	25837	387.04			
15.....	3	25864	386.64						
16.....	2	25880	386.40						
17.....	5	25940	385.51	9	25941	385.49	5	25920	385.8
18.....	2	26008	384.50						
19.....	3	26046	383.94	10	26044	383.97	6	26080	383.4
20.....	2	26066	383.64						
21.....	2	26090	383.28						
22.....	2	26123	382.80						
23.....	3	26161	382.25	11	26168	382.15			
24.....	4	26196	381.74						
25.....	4	26256	380.87						
26.....	5	26295	380.30	12	26300	380.23	7	26280	380.5
27.....	4	26325	379.87						
27 ¹ / ₂	I	26385	379.00						
28.....	2	26411	378.63						
29.....	3	26448	378.10	13	26445	378.14			
30.....	3	26515	377.15	14	26528	376.96			
31.....	2	26547	376.69						
32.....	3	26590	376.08						
33.....	2	26610	375.80						
34.....	5	26645	375.30						
35.....	5	26661	375.08	15	26663	375.05			
36.....	5	26696	374.59						
37.....	3	26720	374.25				8	26730	374.1
38.....	5	26760	373.69	16	26765	373.62			
39.....	4	26783	373.37						
40.....	3	26827	372.76						
41.....	3	26853	372.40	17	26837	372.62			
42.....	2	26880	372.02						

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

REGION OF 2.6 μ —*Continued*

15,000-LINE GRATING				7500-LINE GRATING			HILGER BRASS GRATING		
Band No.	Relative Intensity	Wave-Length A	Wave No. per mm	Band No.	Wave-Length A	Wave No. per mm	Band No.	Wave-Length A	Wave No. per mm
43.....	4	26930	371.33	18	26936	371.25			
44.....	1	26974	370.73						
45.....	3	27006	370.29	19	27002	370.34			
46.....	1	27044	369.77						
47.....	4	27084	369.22	20	27093	369.10			
48.....	4	27103	368.96						
49.....	3	27168	368.08						
50.....	5	27198	367.67	21	27193	367.74	9	27180	367.9
51.....	5	27236	367.15						
52.....	1	27278	366.60						
53.....	1	27294	366.38						
54.....	1	27314	366.11						
55.....	3	27340	365.76						
56.....	5	27386	365.15	22	27395	365.03			
57.....	5	27407	364.87						
58.....	2	27445	364.37				10	27430	364.6
59.....	2	27479	363.91						
60.....	2	27511	363.49						
61.....	5	27545	363.04	23	27544	363.06			
62.....	4	27614	362.14	24	27623	362.02	11	27620	362.0
63.....	3	27625	361.99						
64.....	3	37655	361.60						
65.....	3	27668	361.43						
66.....	3	27700	361.01						
67.....	3	27712	360.85						
68.....	2	27765	360.17	25	27784	359.92			
69.....	2	27777	360.01						
70.....	2	27803	359.67						
71.....	2	27819	359.47	26	27866	358.86			
72.....	3	27867	358.85						
73.....	1	27926	358.09						
74.....	1	27947	357.82						
75.....	1	27972	357.50						
76.....	4	28020	356.77	27	28031	356.75	12	28030	356.8
77.....	2	28077	356.16						
78.....	1	28103	355.83						
79.....	2	28140	355.37						
80.....	3	28197	354.65	28	28198	354.64			
81.....	2	28267	353.77						
82.....	2	28336	352.91	29	28348	352.76	13	28350	352.7
83.....	2	28373	352.45						
84.....	2	28485	351.06						
85.....	2	28538	350.41	30	28540	350.38	14	28540	350.4
86.....	1	28590	349.77						
87.....	1	28658	348.94	31	28710	348.31			
							15	28990	344.9
							16	29210	342.4
							17	29750	336.1

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

PART OF THE REGION OF $6\ \mu$

Hilger brass grating

Band No.	Wave Length λ	Wave No. per mm	Distance from Center, 159.6	Mean Distance of One Pair
1.....	50220	199.1	39.5	
2.....	50850	196.7	37.1	
3.....	51110	195.7	36.1	
4.....	51490	194.2	34.6	
5.....	51720	193.4	33.8	
6.....	52040	192.2	32.6	
7.....	52420	190.8	31.2	
7'.....	52600	190.1	30.5	
8.....	52800	189.4	29.8	
9.....	52960	188.8	29.2	
9'.....	53090	188.4	28.8	
10.....	53520	186.8	27.2	
11.....	54240	184.4	24.8	
11'.....	54470	183.6	24.0	
12.....	54660	182.9	23.3	
13.....	55250	181.0	21.4	
13'.....	55570	179.9	20.3	
14.....	55810	179.2	19.6	
15.....	56170	178.0	18.4	
16.....	56430	177.2	17.6	
17.....	56800	176.1	16.5	
17'.....	56920	175.7	16.1	
18.....	57170	174.9	15.3	
18'.....	57470	174.0	14.4	
19.....	57680	173.4	13.8	
20.....	58240	171.7	12.1	12.2
20'.....	58640	170.5	10.9	10.8
21.....	58830	170.0	10.4	
21'.....	58950	169.6	10.0	0.0
22.....	59380	168.4	8.8	8.8
22'.....	59720	167.5	7.9	7.9
23.....	59880	167.0	7.4	7.4
24.....	60160	166.2	6.6	6.4
25.....	60480	165.3	5.7	5.6
26.....	60720	164.7	5.1	
27.....	61140	163.6	4.0	3.9
27'.....	61440	162.8	3.2	3.2
28.....	61620	162.3	2.7	2.7
29.....	61880	161.6	2.0	2.0
30.....	62160	160.9		
30'.....	62420	160.2		
31.....	62720	159.4		
31'.....	62890	159.0		
32.....	63440	157.6	2.0	
33.....	63740	156.9	2.7	
33'.....	63930	156.4	3.2	
34.....	64180	155.8	3.8	
35.....	64530	155.0	4.6	
36.....	64950	154.0	5.6	
37.....	65200	153.4	6.2	
38.....	65510	152.6	7.0	

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

PART OF THE REGION OF $6\ \mu$ —*Concluded*

Hilger brass grating

Band No.	Wave-Length Å	Wave No. per mm	Distance from Center, 159.6	Mean Distance of One Pair
39.....	65730	152.1	7.4	
40.....	65940	151.7	7.9	
41.....	66340	150.7	8.9	
42.....	66810	149.7	9.9	
43.....	67160	148.9	10.7	
44.....	67520	148.1	11.5	
45.....	67920	147.2	12.4	
46.....	68280	146.5	13.1	

V. QUESTIONS OF INTERPRETATION

In addition to her work with water-vapor mentioned above, Eva von Bahr¹ has studied the absorption of HCl in the neighborhood of $3.5\ \mu$. The combination principle, with the quantum distribution of rotation-frequencies, has been applied by Bjerrum² to set forth reasons for the presence of these absorption bands of HCl and to calculate directly the size of energy quanta. However, the chaotic arrangement of water bands in the region of $2.6\ \mu$, as they appear in Fig. 5, does not appear to satisfy the demands of these hypotheses, though the region has in a general way a center and a rough appearance of symmetry. Since this work was completed Mr. E. H. Imes has mapped the absorption of HCl at $3.5\ \mu$ with the apparatus here described, using an interval of about 30 Å in the slit of the thermopile. The wave-lengths are precisely determined by the grating, and a parabolic shift of the vibration-frequency with increasing rotation-frequency is very definitely displayed. Work on HCl showing this effect has been published by Kemble and Brinsmade,³ though that done here was completed before their work appeared. The curve of Fig. 5 does show a crowding together of bands in the nearer end, which our experience with HCl would lead us at least to consider possible. But the uncertainty, due to

¹ *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 1150, 1913.

² *Ibid.*, **16**, 614, 1914.

³ *Proceedings of the National Academy of Sciences*, **3**, 420, 1917.

the general complexity of the curve, as to which band should be associated with any other to make a pair, and about the location of the vibration center for no rotation, has so far deferred our explanation. The third rotation series mentioned in connection with the work of Rubens and Hettner may perhaps be appealed to as a probable cause of the complexity both at 2.6 and $6\ \mu$.

The appearance of the curves, particularly of Fig. 5, suggests that useful knowledge may be still further advanced by an increase in dispersion. In the case of the $2.6\ \mu$ region, however, neither a finer nor a larger grating would serve this purpose; but a source of greater energy, or a more sensitive detector, would enable us to use narrower slits. We hope to profit by the use of a tungsten ribbon lamp in place of the glower. We may be able to build another more sensitive galvanometer.

It should be pointed out that the selective atmospheric absorption near 2.6 and $6\ \mu$ may account for the unexpected weakness or even the non-appearance of bright lines predicted by the laws of series in the spectra of elements.

It is hoped to employ the apparatus in the further study of absorption, and it may be that the behavior of carbon dioxide will help to explain that of water-vapor. The work here described was undertaken at the suggestion of Professor H. M. Randall, to whom the author makes grateful acknowledgment of his indebtedness.

UNIVERSITY OF MICHIGAN, PHYSICS LABORATORY

September 25, 1917

THE INFRA-RED ARC SPECTRUM OF IRON

H. M. RANDALL AND E. F. BARKER

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THE INFRA-RED ARC SPECTRUM OF IRON

BY H. M. RANDALL AND E. F. BARKER

Captain W. de W. Abney,¹ in 1881, in mentioning his failure to photograph the infra-red arc spectrum of iron, concluded that only those metals which volatilize at low temperature possess an infra-red spectrum. In 1912 H. Lehmann² published the infra-red emission spectra of numerous elements obtained by the phosphorescent method, the extreme wave-lengths being about 15,000 Å. Here the infra-red spectra were most successfully photographed for the easily volatilized substances, while no lines were found for iron. In the photographic region Geiger³ has obtained results extending nearly to 1 μ . The four wave-lengths which he gives beyond 0.9 μ have, however, not been verified by the present investigators. It would appear that he had attempted to extend his measurements beyond the proper limits of his observational method. More recently K. Burns⁴ has worked in the photographic infra-red region, his published values extending to 0.9 μ . In this same region Meggers and Kiess⁵ have recently obtained excellent results beyond 0.9 μ , and some of their values in that region have been included in our tables. The region covered in the present investigation extends from 9000 to 30,000 Å and has been found to contain some fifty measurable lines. Iron was found to be a difficult material to work with, the first attempts being very unpromising, but gradually the conditions necessary for the production of an infra-red spectrum sufficiently intense and steady for bolometric measurement were learned, so that in the region covered the infra-red iron spectrum is at present the richest in the number of its measured lines. As a large majority of these lines are weak, it is evident that the iron spectrum preserves in this region the characteristics of its photographic region. The extent and distribution of this

¹ *Proceedings of the Royal Society*, **32**, 343, 1881.

² *Annalen der Physik*, **39**, 53, 1912.

³ *Ibid.*, **39**, 782, 1912.

⁴ *Lick Observatory Bulletin*, **9**, 27, 1913.

⁵ *Scientific Papers of the Bureau of Standards*, No. 324, June 1918.

long-wave spectrum, together with the exactness of the measurements now possible, suggest that an attempt to extend the work of Gale and Adams¹ on the pressure-shift of iron lines into the infra-red might meet with success. Should any of the lines in the neighborhood of 25,000 Å belong to their *a* group and the law hold that the shift with pressure varies as the third power of the wave-length, there should be a change in the wave-length of over 4 Å for an increase in pressure of 10 atmospheres, while lines of the *d* group would show a shift of more than 17 Å. As it is probable that shifts of 1 Å would be readily observed under conditions easily obtainable, it is evident that it is now possible to extend investigations of pressure-shifts of arc lines into the infra-red region.

As the experimental arrangement of the mirror spectrometer by which the line spectrum of the iron, produced by a grating, is passed over the slit of a linear thermopile has been described in an earlier paper,² it will not be discussed here. The methods of observation are also essentially the same. The grating was that used in previous work and was kindly lent us by Professor Hussey, of the Detroit Observatory. It is a flat six-inch grating with 15,000 lines per inch, ruled by Dr. Anderson, and has given very good service. The slits of collimator and thermopile were at first approximately 0.2 mm wide and covered a spectral region in the neighborhood of 1 μ of about 6 Å, and at 3 μ of 3.6 Å. Later the entire spectrum was examined with a slit 0.5 mm wide, and a very appreciable number of weaker lines were found and measured. No systematic differences between the values of wave-lengths measured with the slits of different width were noticed.

Through the kindness of Professor Campbell, of the department of chemistry, we obtained the American ingot iron with which the major part of the work was done. This iron is over 99.8 per cent pure, the largest single impurity being copper, which is present in the proportion of approximately 0.04 per cent. We also obtained through the courtesy of Professor Terry, of Wisconsin, a sufficient quantity of Burgess electrolytic iron to check up the results obtained with the other iron. None of the impurities, found in small

¹ *Astrophysical Journal*, 35, 10, 1912.

² H. M. Randall, *Astrophysical Journal*, 34, 1, 1911.

traces only in both irons, were found to give lines; in fact, as later experience has shown, iron less pure would probably have sufficed, as it is only when there are large quantities of volatilized metal present in the arc that the lines appear with sufficient intensity to be measured.

The iron was placed in a boring in the positive carbon, the diameter of the hole being as large as the three-quarter-inch carbon would permit. To secure greater localization of heat in the metal the carbon was occasionally nearly sawed off immediately below the boring. The carbons used showed the several infra-red K lines and also two others, whose approximate values are 11,439 Å and 10,692 Å. As these values do not correspond to any infra-red lines previously measured their origin is at present unknown.

The currents necessary to volatilize the metal sufficiently to produce measurable lines from the point of view of intensity and steadiness were very large, in general in excess of 60 amperes. Lines which are broadened unsymmetrically may very well have their measured values appreciably altered by the use of such currents, as was shown in earlier work, particularly with caesium,¹ although more recently² several barium lines capable of measurement with relatively small currents gave substantially the same values for all currents. At present there seems to be no way of avoiding large currents, and any estimation of the accuracy of determinations of wave-length must be qualified through this possibility of unsymmetrical broadening which cannot be allowed for in bolometric measurements on arc lines. Recently the inclusion of a very large inductance in the circuit has very effectively prevented the frequent extinction of the arc during observations.

The wave-lengths given in the table are in angstrom units as measured in air according to the Rowland scale, the spectrometer being calibrated with the Hg line 10,140.15 Å as measured by Volks.³ The intensities of the lines are indicated by the mean of the galvanometer deflections in millimeters of the separate determinations, two or more in number, when the 0.5 mm slit was used.

¹ H. M. Randall, *Astrophysical Journal*, **34**, 12, 1911.

² *Ibid.*, **42**, 200, 1915.

³ Inaugural Dissertation, Tübingen, 1914.

These numbers given in the first column of the table are at best but a very rough indication of the relative intensities of the lines, as the deflections for any one line vary between wide limits, depending upon the state of the arc, which is always very unsteady. The column headed "Maximum Variation from Mean" will give a good idea of the reproducibility of results by the methods here used, as the values are those obtained independently by two observers working at different times, the apparatus having been dismantled and otherwise used in the meantime. In general, unless otherwise stated, the values given are considered correct to within 1 or 2 Å. This estimate has been verified whenever more accurate methods have furnished standards for comparison. In the present work six lines between 0.8μ and 1μ , measured two or more times, show a mean variation from values obtained photographically by Meggers and Kiess of 0.9 Å , the maximum single difference being -1.9 Å . This is the region of the spectrum where the bolometric method is least accurate. The smaller dispersion of the grating here, together with the intensity of the general radiation in the neighborhood of 1μ , produces a strong background of rapidly varying intensity, so that the location of lines superimposed upon it becomes very difficult. For the region between 0.8μ and 1μ the photographic method is the more sensitive, yielding more lines; the lines so measured should be more accurate than can be obtained by our method. Beyond 1μ , however, the bolometric method apparently becomes increasingly the more sensitive, and accordingly our values in and beyond this region become increasingly the more reliable.

A number of the lines marked with asterisks have been measured but once, two years ago this summer. They were not found a year later when an attempt was made to measure them. While the measurements, when made, were so normal in all respects that we have great confidence in the lines, still the fact that they were not found again places them somewhat in doubt. The two strongest of the lines in this region, $25,987 \text{ Å}$ and $26,229 \text{ Å}$, were found and remeasured last year, which strengthens the view that conditions at the first measurement were particularly favorable to the formation of a spectrum, and that for some reason it was not possible to reproduce those conditions.

In a spectrum so rich in lines as that of iron it will naturally occur that a number of the infra-red lines will coincide, within the limits of accuracy obtainable in these measurements, with the higher orders of shorter lines. When the shorter lines are weak

Int.	Wave-Length, Rowland Scale	No. of Deter- minations	Maximum Va- riation from Mean	Remarks	Int.	Wave-Length, Rowland Scale	No. of Deter- minations	Maximum Va- riation from Mean	Remarks
50...	9001.1 A	3	1.1 A	(a)	15...	14710.7 A	2	0.2 A	
40...	9090.3	2	0.8	(b)	10...	14744.2	2	0.5	
20...	9210.4	3	2.3	(c)	20...	14828.2	3	0.9	
20...	9257.1	3	2.0	(d)	20...	15054.2	3	0.8	
20...	9407.8	2	0.6	(e)	35...	15212.5	2	0.5	
15...	9740.0	3	1.4		70...	15295.7	4	0.9	
15...	10063.3	2	1.7	(f)	30...	15396.4	3	0.6	(j)
30...	10144.3	4	2.7		25...	15624.8	2	0.5	
20...	10216.0	3	2.1		40...	15771.2	2	0.6	
20...	11608.0	3	1.0		25...	15815.1	3	0.6	
25...	11640.8	2	0.1		25...	15820.8	2	0.5	
50...	11884.2	4	0.8		15...	16165.9	2	0.1	
75...	11974.7	3	0.9		15...	16317.2	2	0.5	
25...	12033.5	2	0.8		10...	16397.2*	1		
45...	13564.1	2	0.9		15...	16494.6*	1		
50...	13899.4	2	1.4	(g)	10...	16608.0*	1		
10...	13978.5	2	0.1		10...	18856.2*	1		
15...	14124.4	2	0.6		5...	25341.5*	1		(k)
40...	14237.1	4	2.1	(h)	15...	25661.5*	1		
40...	14287.9	4	1.6		25...	25987.4	2	0.3	
100...	14401.8	3	0.4		20...	26229.4	2	1.1	
20...	14440.4	3	2.7	(i)	5...	26487.3*	1		
75...	14513.3	3	0.5		5...	26727.4*	1		
35...	14558.3	4	1.8						

EXPLANATION OF REMARKS

- (a) Meggers and Kiess value reduced to Rowland scale 8999.8 A.
 (b) Meggers and Kiess 9089.1 A, mean of two near lines.
 (c) Possible error ± 3 A, Meggers and Kiess 9210.41.
 (d) Possible error ± 3 A, Meggers and Kiess 9259.0, mean of two near lines.
 (e) Meggers and Kiess 9407.9, mean of two near lines. Meggers and Kiess 9739.0.
 (f) (The foregoing means are weighted means, each line being weighted according to its estimated intensity.)
 (g) Possible error ± 3 A.
 (h) Possible error ± 3 A.
 (i) Possible error ± 3 A.
 (j) Absorption by water too complete to be 2d order of K7699.4 (10).
 (k) Possibly 4th order 6336.

their higher orders do not produce effects which are measurable radiometrically. With the strong lines absorbing screens have been used when possible to eliminate effects of higher order. In other instances the complete absorption of the observed lines by varying thicknesses of water and glass have shown them to be first-order lines of long wave-length. While some of the results in the foregoing table appear to be second orders of strong lines, it is thought, nevertheless, that in each case the effect measured is that of a superposed first-order line.

We have been very materially assisted in part of this work by Mr. Jean Cooley, whose aid was made possible through a grant by the American Academy of Science, to which we wish to acknowledge our indebtedness.

PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN
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THE INFRA-RED ARC SPECTRA OF COBALT, NICKEL, MANGANESE, AND CHROMIUM

H. M. RANDALL AND E. F. BARKER

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THE INFRA-RED ARC SPECTRA OF COBALT, NICKEL, MANGANESE, AND CHROMIUM

By H. M. RANDALL AND E. F. BARKER

Measurements in the infra-red region of the spectrum have yielded such fruitful results in developing the series relations of numerous elements that the major part of the work in this field has been done for this express purpose. There remain, however, the same general reasons for mapping out the spectra of all elements beyond the photographic region on the side of long wave-lengths as exist for the numerous investigations within that region. As it seemed probable that the technique developed during the measurement of the infra-red spectrum of iron¹ would serve equally well for the allied metals, cobalt, nickel, manganese, and chromium, it was decided to continue the work with these elements. The experimental arrangement remained the same, as did also the experimental methods. With the exception of manganese, which volatilized readily and gave a comparatively steady arc which yielded the strongest lines of any of the metals of this group, the metals were very similar to iron in their action in the arc. Nickel and cobalt produced possibly an even more uncertain arc than iron. While it would not be easy to say wherein the differences lay, it was nevertheless the experience of both observers that a certain amount of facility in using each substance in the arc was necessary before an arc of an intensity and steadiness sufficient for observation would result.

The materials used were the ordinary c. p. metals of commerce. This degree of purity seems at present sufficient, as no lines due to any of the impurities likely to be found in the samples used were actually found. In fact a large majority of the lines appeared sufficiently intense for measurement only when a fairly large quantity of material was in the arc and there was obviously excessive volatilization, the arc burning very noisily. The currents employed were again large, being in general between 60 and 80 amperes.

¹ Randall and Barker, "Infra-Red Arc Spectrum of Iron," *Astrophysical Journal*, 49, 42, 1919.

The spectrum of each material was in general twice searched, once with narrow slits corresponding to a spectral region before the thermopile of from 6 Å at $1\ \mu$ to 3.6 Å at $3\ \mu$, and once with double slit-widths. With cobalt the region covered extended from $0.9\ \mu$ to $2\ \mu$; with nickel from $0.9\ \mu$ to $3\ \mu$; the region between $2\ \mu$ and $3\ \mu$, however, was gone over but once. With manganese the region from $0.9\ \mu$ to $2\ \mu$ was covered twice and from $2\ \mu$ to $3\ \mu$ once; with chromium from $0.9\ \mu$ to $3\ \mu$ twice.

NICKEL

Wave-Lengths Rowland Scale	Maximum Variation from Mean	Intensity	Number of Determinations	Remarks
8967.5.....	0.0	100	2 ^a	Meggers and Kiess 9520.3
9522.1.....	0.0	40	2	
10195.1.....	1.5	50	3	
10301.4.....	0.0	25	2	
10330.0.....	0.7	25	2	
10378.1.....	1.0	40	3	
10980.4.....	0.3	50	2	
11198.1.....	0.0	35	2	
11591.1.....	2.0	30	3	
13553.7.....	0.2	20	2	
13722.6.....	0.5	50	2	Possible error $\pm 3\ \text{\AA}^\circ$
13829.6.....	1.5	30	3	
13969.0.....	0.2	20	2	
14102.1.....	0.3	20	2	
14874.7.....	0.5	30	2	
16313.0.....	1.0	15	2	
16363.0.....	0.2	100	2	
16409.4.....		50	1	
16495.5.....		120	1 ^b	
16868.5.....	0.7	15	2	Very doubtful; could not be verified
16999.6.....	1.4	60	5	
17986.8.....	0.5	20	2	
18040.6.....	0.8	15	2	

^a Meggers and Kiess 8967.3 mean of two near lines on Rowland Scale. A number of lines shorter than 8967.5 show a mean difference of $+0.6\ \text{\AA}$ from Meggers and Kiess values, maximum difference being $1.2\ \text{\AA}$.

^b Doubtful; subsequent search showed more indications of a line. Line of equal value found once in Fe.

In a number of cases the values obtained agree within the limits of experimental error with previously measured lines of other elements. In each case, however, the strongest lines in the spectra of these other elements have not appeared, so that the lines in question have been considered new lines properly belonging to the substance under examination. In the case of manganese

measurements on a number of the lines of greatest intensity were made by our colleague, Dr. Sleator, the results being practically identical with our individual determinations.

COBALT

Wave-Lengths Rowland Scale	Maximum Variation from Mean	Intensity	Number of Determinations	Remarks
9096.5.....	1.2	10	2	M. and K. 9095.8
9357.2.....	0.4	40	2	M. and K. 9357.4
9545.8.....	0.9	100	3	M. and K. 9544.9
9598.4.....	1.4	30	2	M. and K. 9598.3
9661.3.....		20	1	Found but once, doubtful
10046.6.....	3.3	30	3	Possible error $\pm 5 \text{ A}^\circ$
10128.7.....	0.1	15	2	
10170.7.....	1.9	20	3	
10359.1.....	3.9	15	3	Possible error $\pm 5 \text{ A}^\circ$
10689.7.....	0.2	40	2	
11633.5.....	0.3	20	2	
11894.5.....	0.5	10	2	
14062.0.....	1.7	40		
14559.0.....	0.6	15	2	
14610.9.....	0.0	35	2	
14680.9.....	0.6	20	3	
14958.0.....	1.0	30	2	
15209.6.....	1.2	15	2	
16132.6.....	0.3	50	3	
16256.9.....	2.1	50	3	Possible error $\pm 3 \text{ A}^\circ$
16387.5.....	1.5	30	3	
16447.2.....	1.4	20	2	
16573.8.....	0.2	30	2	
17004.9.....	0.3	50	2	
17080.4.....	2.6	30	3	Possible error $\pm 5 \text{ A}^\circ$
18175.5.....	0.8	30	2	
18273.8.....	0.4	20	2	
19778.7.....	0.0	30	2	

In the case of chromium there are between 0.9μ and 1.3μ twenty-five measurable lines, while in the corresponding region of manganese there are but six lines, the region between 0.9μ and 1μ being entirely free, a very remarkable fact in view of the richness of this region for nearly all materials so far examined. In manganese in the interval from 1.3μ to 1.7μ are found fifteen lines, the majority of its entire number, while the corresponding region for chromium is quite empty, there being but two or three lines. From 1.7μ onward chromium has sixteen lines, while manganese has shown no lines of measurable intensity. This alternate arrangement of the spectra of these nearly related elements

is rather striking, though probably without special significance. It is noticeable that there is in chromium, as in the case of iron, a group of lines found in the region of 2.5μ upon which but a single measurement has been made. These measurements were in every way normal and all the lines showed complete absorption by a

MANGANESE

Wave-Lengths Rowland Scale	Maximum Variation from Mean	Intensity	Number of Determinations	Remarks
8672.3.....	1.1	80	3	
8703.1.....	0.6	100	2	
8739.9.....	0.4	80	2	
11378.4.....	0.0	15	2	
11614.4.....	2.0	40	5	
11782.8.....	2.7	60	4 ^a	Possible error $\pm 3 \text{ \AA}$?
12307.9.....				Very doubtful; not found a second time
12900.3.....	1.4	80	4	
12976.5.....	0.9	40	5	
13294.7.....	1.1	50	3	
13318.5.....	0.6	30	5	
13416.5.....	0.5	80	2	
13500.7.....	1.3	100	3	
13626.3.....	1.8	200	6	
13685.2.....	0.2	80	2	
13864.4.....	1.6	100	5	
13997.6.....	1.6	120	5	
14970.5.....	3.8	30	4	Possible error $\pm 3 \text{ \AA}$
15218.6.....	0.5	80	3	
15263.8.....	0.8	200	3	
15965.6.....	1.5	200	3	
17336.0.....	0.6	80	2	
17608.3.....	1.0	20	3	

^a Value possibly influenced by 11771.7 K, carbon impurity.

water screen 1 cm thick. We have therefore considerable confidence in their reality but can give them here only provisionally, as we have been unable to find them a second time. It might be noticed that this group, as well as the one in iron whose members could not be measured at will, lies in the absorption band of water vapor at 2.5μ , and that during the summer months the basement-room in which the work was carried on was comparatively damp. As by our optical arrangement the radiation from the arc passes through about 3 m of air it is quite possible that considerable energy is absorbed by the intervening vapor.

In the tables the mean of the observed values appears in the first column measured in angstrom units. The values when not

CHROMIUM

Wave-Lengths Rowland Scale	Maximum Variation from Mean	Intensity	Number of Determinations	Remarks
8947.3.....	0.3	160	2	Meggers value on Rowland scale 8947.5
8977.1.....	0.4	30	2	Meggers value on Rowland scale 8977.1
9015.4.....	2.8	300	6 ^a	
9140.6.....	0.7	20	2	
9206.3.....	2.0	30	3	
9290.6.....	1.6	150	4	Meggers value 9290.8
9447.9.....	0.6	150	3	
9574.6.....	1.2	150	3	
9670.9.....	1.1	50	4	
9732.2.....	1.5	120	5	
9948.4.....	1.1	20	4	
10082.0.....	0.9	20	2	
10486.3.....	1.3	35	2	
10673.4.....	0.6	30	2	
10819.9.....	0.8	40	2	
10906.2.....	1.3	60	4	
11016.0.....	2.9	80	5	Possible error ± 4 A
11157.6.....	1.4	90	6	
11311.9.....	0.7	20	2	
11337.1.....	0.6	40	2	
11392.3.....	2.6	50	5	Possible error ± 3 A
11483.3.....	1.0	40	2	
11611.4.....	0.8	100	5	
13462.1.....		20	1	
15680.0.....	3.7	30	4	Possible error ± 3 A
15860.5.....	0.6	30	3	
18479.1.....	4.1	30	3	Possible error 5 A
18583.5.....	1.6	30	4	
18654.2.....	1.1	30	2	
18717.0.....	0.5	20	2	
25459.6*.....		15	1	
25489.7.....		10	1	
25560.4.....		10	1	
25583.6.....		20	1	
25665.4.....		10	1	
25708.8.....		10	1	
25784.6.....		5	1	
25819.6.....		10	1	
25849.7.....		20	1	
25902.2.....		10	1	
26232.0.....		20	1	

^a Broad line. Possible error 4 A. Meggers value 9016.5 (Mean).

* The following lines are to be considered doubtful until verified.

otherwise stated are supposed to be accurate within one or two angstrom units. The intensities are determined by a very rough

mean of the galvanometer deflections during measurement. They have some significance as rating the intensities of the lines of any one element, but have very little as a means of comparison of intensities between lines of various elements.

A number of the lines in the tables are multiples of strong lines of short wave-length. It is thought, however, that in each case it has been established that the higher-order line of short wave-length is superposed by a line of long wave-length of the first order. In some cases, where it has not been possible to screen out the line of higher order, it is quite probable that its presence has somewhat affected the value ascribed to the line under observation.

As an infra-red region up to $1\ \mu$ was regarded as properly within the field of photographic methods, only a superficial examination of this region was made in this work. This largely accounts for the fact that we have not measured all the strong lines which the recent work of Meggers and Kiess shows to be here. Such lines as we have measured, as the comparisons in the tables show, have a somewhat higher accuracy than we have claimed for them, taking the photographic values as standards. The mean departure of all our measured lines below $1\ \mu$, 19 in number, including quite a number of lines shorter than $0.9\ \mu$ not contained in the tables, is $0.6\ \text{\AA}$, while the maximum variation is $1.9\ \text{\AA}$. The superiority of the photographic method in registering faint lines is made very evident by these investigations, and it may be safely concluded that, except possibly in special cases, the infra-red spectrum up to $1\ \mu$ is properly a photographic region.

Surprisingly enough, the same cannot yet be said of the region immediately beyond $1\ \mu$, in which photographic observations have been taken with apparently as great success, in the case of Ni to $10,843\ \text{\AA}$, Co to $11,623\ \text{\AA}$, and Fe to $10,689\ \text{\AA}$. A comparison of the results obtained photographically and radiometrically shows no cases which are unquestionably in agreement, though there are in the foregoing regions twelve radiometrically determined lines and many more photographic lines.

Confidence in radiometric measurements in this region is based upon the following general considerations: The radiometric methods here employed, as well as that earlier used by Lewis,¹

¹ *Astrophysical Journal*, 2, 1, 106, 1895.

which is similar, have given values between 0.7μ and 1μ , which have been substantiated by subsequent photographic results. The results under comparison are in fact an instance of such a confirmation. The same lines beyond 1μ have been measured by different observers using different gratings and making determinations in higher orders for the strong lines with closely agreeing results, and finally with those substances for which there are series relations there have been numerous instances in which the radiometric values beyond 1μ have so perfectly met the requirements that the confidence in their accuracy has become very great.

Since the particular lines in question have been measured under usual conditions of observation and have shown no peculiarities during observations, but have, on the other hand, been quite normal in all respects, there appears to be no reason for questioning their accuracy. In this work also we wish to express our indebtedness to the American Academy of Arts and Sciences for a grant from the Rumford fund which enabled us to obtain the services of an assistant.

PHYSICAL LABORATORY
UNIVERSITY OF MICHIGAN

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